

Laser-induced steric effects in nonlinear processes from short laser pulses

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The response of a diatomic or symmetric-top molecule in a nonlinear optical process through its third-order susceptibility is investigated in terms of the internuclear axis orientation and the plane of molecular rotation. The effect of the spatial arrangement of the molecular system in a Raman-type or two-photon absorption-type intermediate resonance is studied for laser pulses having a time-duration short compared to a simple molecular rotation. We observe strong steric effects on the internuclear axis angular distribution depending drastically on the resonant rotational structure and on the incident polarizations. [S1050-2947(96)01009-8]

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I. INTRODUCTION

Due to the importance of resonance enhancement and angular momentum conservation, the investigation of spectroscopic properties in nonlinear optical processes have yielded a great amount of information on the molecular structure. In a nonlinear optical process, incident photons can be destroyed and a scattered photon created while the molecule undergoes a transition from an initial state to a final state. This process is coherent in the sense that these three events are interdependent and thus cannot be resolved [1,2]. An interesting feature derives from this fact since for nonlinear optical processes the scattering time may be very fast compared to the molecular rotational period. This allows one to investigate the internuclear axis angular distribution of the molecular susceptibility of a free-rotating molecule in a nonlinear process provided that the laser pulse time duration is short compared to a simple molecular rotation.

Experimental conditions implying an interaction time shorter than a simple molecular rotation may occur in various situations [3,4]. For instance, nonresonant electronic processes may reach characteristic response times of the order of 10^{-15} s whereas the rotational period of molecules is typically of the order of 10^{-10} – 10^{-11} s. Moreover, when the incident frequency in a Raman resonance is above a dissociation limit the reemission time may be limited only by the time needed for the atoms to fly apart, under these circumstances the scattering time can be smaller than one picosecond. Finally, it is worth noting that coherent anti-stokes Raman-scattering (CARS) processes can be carried out equally well with picosecond lasers and thus may be easily used as a diagnostic tool for very fast relaxation processes.

There are extensive investigations on orientation and alignment effects related to the angular momentum [5–7]. Orientation for the internuclear axis in a selected rotational level has been obtained with NO molecules by exploiting the permanent electric dipole of this molecule in conjunction with the Stark effect and using strong hexapole electric fields [8]. More recently it has been shown that an intense laser field forces all molecules to align along its polarization vector [9]. In this high-field limit pendular states are present similar to those for permanent dipoles subject to static fields [10]. To date, however, there is a lack of theoretical and experimental results concerning the effect of orientation or

alignment of the internuclear axis during the excitation time interval. It is worth pointing out that a well-prepared internuclear axis selected excited state is a crucial parameter for the analysis and understanding of the dynamics of many processes. In particular, the oriented molecules in a neutral excited state can subsequently react with an atomic, molecular, or laser beam and furnish detailed information on the internuclear axis angular dependence of the reactivity, photodissociation, or photoionization of this state. In such circumstances the spatial arrangement of the molecular system in the excited state needs to be a controlled parameter and, under this aspect, the sensitivity and the short duration of the probing pulses in conjunction with the state selectivity due to energy and angular momentum conservation make the nonlinear processes promising in the study of photofragments and fast relaxation processes.

In this work we consider the internuclear axis steric effect induced in a nonlinear optical process when a short excitation time interval is involved. In what follows we assume that a diatomic or symmetric-top molecule is found initially in some electronic-vibrational state occupying one or more rotational states which are well described by Hund's case a coupling. The frequent case of singlet transitions in diatomic molecules is then deduced as a particular case.

For a short laser pulse the spectral bandwidth may be quite large implying the simultaneous excitation of multiple rotational lines. Therefore, as long as adjacent initial rotational states are populated their relative occupation probability should be taken into account. As a particular case the laser induced steric effect is investigated for a thermal distribution of the initial rotational states. Due to the orientation dependence of the excitation process an anisotropic selection for the internuclear axis is expected to take place. The elucidation of this point is the major focus of this work.

II. INTERNUCLEAR AXIS AND ANGULAR MOMENTUM ORIENTATION DEPENDENCES

We consider the third-order molecular susceptibility with an intermediate resonance with the second photon, the two-photon resonance may be either Raman or a two-photon absorption-type resonance. It can be seen that under these circumstances any nonlinear process can be deduced from the tensor [11]

$$\begin{aligned} \chi_{p_1'p_2'p_2p_1}^{(3)}(-\omega_1' - \omega_2'\omega_2\omega_1) &= \frac{N}{6\hbar} \left(\frac{1}{\omega_{eg} - \omega_2 - \omega_1 - i\Gamma_{eg}} \right) \\ &\times \sum_{\text{deg } eg} (\rho_{gg}^{(0)} - \rho_{ee}^{(0)}) (\alpha_{eg}^{-p_2'-p_1'}) \\ &\times (\omega_2'\omega_1')^* (\alpha_{eg}^{p_2p_1}(\omega_2\omega_1)), \end{aligned} \quad (1)$$

where g stands for the initial state and e for the two-photon resonant state. The sum extends over all degenerated molecular states and $\rho_{gg}^{(0)}$ and $\rho_{ee}^{(0)}$ are the unperturbed diagonal density-matrix elements for state g and e ; respectively. N is the number density of molecules. In the above expression the tensor $\alpha_{eg}^{p_2p_1}(\omega_2\omega_1)$ is the first-order hyperpolarizability tensor, we have

$$\begin{aligned} \alpha_{eg}^{p_2p_1}(\omega_2\omega_1) &= \frac{1}{\hbar} \sum_i \left(\frac{\langle \vec{\epsilon}_{p_1} \cdot \vec{\mu} | i \rangle \langle i | \vec{\epsilon}_{p_2} \cdot \vec{\mu} | g \rangle}{\omega_{ig} - \omega_2} \right. \\ &\left. + \frac{\langle e | \vec{\epsilon}_{p_2} \cdot \vec{\mu} | i \rangle \langle i | \vec{\epsilon}_{p_1} \cdot \vec{\mu} | g \rangle}{\omega_{ig} - \omega_1} \right), \end{aligned} \quad (2)$$

where $\vec{\mu}$ is the electric dipole moment operator, $\vec{\epsilon}_p$ is the unit polarization vector, and the summation extends over all intermediate molecular states i .

The particular notation $\chi_{p_1'p_2'p_2p_1}^{(3)}(-\omega_1' - \omega_2'\omega_2\omega_1)$ = $\chi_{p_2'p_1'p_2p_1}^{(3)}(-\omega_2' - \omega_1'\omega_2\omega_1)$, instead of the notation $\chi_{p_1p_2p_3p_4}^{(3)}(-\omega_4; \omega_3\omega_2\omega_1)$, will be adopted throughout this work in order to emphasize the fact that, for all processes, we have an intermediate two-photon resonant state. The resonance of the first two photons, which constitutes the ‘‘starting step’’ of the process, is symbolized by unprimed quantities whereas the primed frequencies and polarizations will be associated with the ‘‘ending step.’’ In particular, out of intermediate single-photon resonances,

$$\begin{aligned} \chi_{-p_1-p_2p_2p_1}^{(3)}(-\omega_1 - \omega_2\omega_2\omega_1) &= \chi_{-p_2-p_1p_2p_1}^{(3)} \\ &\times (-\omega_2 - \omega_1\omega_2\omega_1) \end{aligned}$$

describes the two-photon absorption process whereas $\chi_{-p_s-p_p p_s p_p}^{(3)}(\omega_s - \omega_p - \omega_s\omega_p)$ stands for the stimulated Raman-scattering (SRS) process showing that only the square modulus of the first-order hyperpolarizability tensor is involved. The tensor $\chi_{p_{as}p_1p_2p_1}^{(3)}(-\omega_{as}\omega_1 - \omega_2\omega_1)$ describes the coherent anti-Stokes Raman scattering (CARS) process.

Since the molecular wave functions are expressed in terms of molecule fixed frame (MFF) coordinates and not in terms of laboratory fixed frame (LFF) coordinates one has to transform the LFF electric dipole components $\mu_p = \vec{\epsilon}_p \cdot \vec{\mu}$ into the MFF. In the MFF, where the rotational motion is absent, the basis set wave functions are the wave functions $|aL\Lambda S\Sigma\rangle$ with a denoting the remaining quantum numbers necessary to describe the molecular state under consideration. In the LFF, however, the rotational motion is present and we have the basis set $|aL\Lambda S\Sigma\rangle|r\rangle$ with $|r\rangle$ being the rotational wave function. As usual, the rotational motion is slow compared to

the electronic-vibrational motion and we may separate the rotating and the nonrotating part in the molecular wave function [12]. We will also use the fact that for spin allowed transitions the wave function $|aL\Lambda S\Sigma\rangle$ splits into $|aL\Lambda\rangle|S\Sigma\rangle$ since the quantum numbers Λ , S , and Σ are all good and the same orbital wave function $|aL\Lambda\rangle$ is associated with all $2S+1$ spin wave functions $|S\Sigma\rangle$. Therefore, in what follows the complete basis set functions will be assumed as products of a function containing only the variables of the nonrotating molecule and a function containing only the rotational variables [13]. Finally, since the MFF components of $\vec{\mu}$ do not involve the rotational variables, the corresponding matrix elements are diagonal in the rotational quantum number J and thus we need only to consider matrix elements of $\vec{\mu}$ in the nonrotating-molecule basis set. This is to say that the MFF-electric dipole matrix elements will be treated throughout this work as molecular parameters.

In order to separate the orientation and rotational dependence in the molecular susceptibility we consider, first, the transition hyperpolarizability tensor. After inspection of the hyperpolarizability tensor in Eq. (2) one remarks that, since the angular frequency ω_1 (or ω_2) is far from any molecular resonance, the rotational contribution in the energy denominator can be neglected. Then, the energy denominator becomes independent of rotational variables and this allows one to perform the summation over all intermediate rotational states, namely, we use the closure relation $\sum_{r_i} |r_i\rangle\langle r_i| = 1$ and we obtain

$$\alpha_{eg}^{p_2p_1}(\omega_2\omega_1) = \sum_{q_1q_2} \langle r_e | \mathcal{D}_{p_2q_2}^{(1)*} \mathcal{D}_{p_1q_1}^{(1)*} | r_g \rangle \tilde{\alpha}_{e\mathcal{J}}^{q_2q_1}(\omega_2\omega_1), \quad (3)$$

with

$$\begin{aligned} \tilde{\alpha}_{e\mathcal{J}}^{q_2q_1}(\omega_2\omega_1) &= \frac{1}{\hbar} \sum_i \left(\frac{\langle e | \tilde{\mu}_{q_1} | i \rangle \langle i | \tilde{\mu}_{q_2} | \mathcal{J} \rangle}{\omega_{i\mathcal{J}} - \omega_2} \right. \\ &\left. + \frac{\langle e | \tilde{\mu}_{q_2} | i \rangle \langle i | \tilde{\mu}_{q_1} | \mathcal{J} \rangle}{\omega_{i\mathcal{J}} - \omega_1} \right), \end{aligned} \quad (4)$$

the MFF-transition hyperpolarizability for the transitional path q_1q_2 .

We have used the transformation $\mu_p = \sum_q \mathcal{D}_{pq}^{(1)*}(\alpha\beta\gamma) \tilde{\mu}_q$ and the associativity of the rotational matrices [14]. The tilde indicates that the corresponding quantity is taken in the MFF, whereas script style letters are used for the wave functions containing only the nonrotating part. That is, in this expression we have used the abbreviation $|g\rangle = |\mathcal{J}\rangle|r_g\rangle$, $|i\rangle = |\mathcal{J}\rangle|r_i\rangle$ and $|e\rangle = |\mathcal{J}\rangle|r_e\rangle$. Moreover, in order to simplify the notation, the Euler angles $\alpha\beta\gamma$ have been omitted from the rotation matrix elements. Then one obtains an expression connecting the LFF to the MFF-third-order susceptibility, we find

$$\chi_{p_1'p_2'p_2p_1}^{(3)} = \sum_{\substack{q_1'q_2' \\ q_1q_2}} \left(\sum_{\deg(\zeta)} Q(\zeta) \langle r_g | \mathcal{D}_{-p_1'-q_1'}^{(1)} \mathcal{D}_{-p_2'-q_2'}^{(1)} | r_e \rangle \right. \\ \left. \times \langle r_e | \mathcal{D}_{p_2q_2}^{(1)*} \mathcal{D}_{p_1q_1}^{(1)*} | r_g \rangle \right) \tilde{\chi}_{q_1'q_2'q_2q_1}^{(3)}. \quad (5)$$

For simplicity we dropped the frequency dependence since it is the same, both, in $\chi_{p_1'p_2'p_2p_1}^{(3)}$ and $\tilde{\chi}_{q_1'q_2'q_2q_1}^{(3)}$. The sum over $\deg(\zeta)$ takes into account the rotational degeneracy exclusively whereas the letter ζ stands for the abbreviation $J_g M_g \Omega_g; J_e M_e \Omega_e$. $Q(\zeta)$ is a partition function taking into account the relative occupation probability of the unresolved rotational states due to the broad spectral bandwidth of the short laser pulse.

The MFF-susceptibility shown in Eq. (5) is written

$$\tilde{\chi}_{q_1'q_2'q_2q_1}^{(3)} = \frac{N}{6\hbar} \left(\frac{1}{\omega_{eg} - \omega_2 - \omega_1 - i\Gamma_{eg}} \right) \sum_{\substack{d \\ \text{deg } \varrho}} (\rho_{\varrho}^{(0)} \\ - \rho_{ee}^{(0)}) (\tilde{\alpha}_{\varrho}^{-q_2'-q_1'}(\omega_2', \omega_1'))^* (\tilde{\alpha}_{\varrho}^{q_2q_1}(\omega_2, \omega_1)). \quad (6)$$

The quantity $\langle r_g | \mathcal{D}_{-p_1'-q_1'}^{(1)} \mathcal{D}_{-p_2'-q_2'}^{(1)} | r_e \rangle \langle r_e | \mathcal{D}_{p_2q_2}^{(1)*} \mathcal{D}_{p_1q_1}^{(1)*} | r_g \rangle$ contains the rotational, polarization, and transitional path dependences. These matrix elements involve integrations over the Euler angles and thus average over all internuclear axis

orientations. However, when the laser pulse time duration is short compared to a simple molecular rotation one has to take into account the fact that the orientation of the internuclear axis cannot change significantly during the excitation time interval. Also, due to inertial effects, we may assume that this orientation cannot be modified from the laser-molecule interaction and thus reorientation effects can be neglected. On the other hand, for a laser pulse with a time duration long compared to the rotational period one should average over all internuclear axis orientations. If β is the angle describing the orientation of the internuclear axis in the laboratory, the two situations are related as follows:

$$\langle r_g | \mathcal{D}_{-p_1'-q_1'}^{(1)} \mathcal{D}_{-p_2'-q_2'}^{(1)} | r_e \rangle \langle r_e | \mathcal{D}_{p_2q_2}^{(1)*} \mathcal{D}_{p_1q_1}^{(1)*} | r_g \rangle \\ = \frac{1}{2} \int_{\beta=0}^{\pi} \sin \beta d\beta S_{p_1'p_2'p_2p_1}^{q_1'q_2'q_2q_1}(\zeta; \beta). \quad (7)$$

For singlet molecular states or for slow molecular rotation where the rotational wave functions are well described by Hund's case a coupling we may take as rotational wave function the expression

$$|r\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} e^{-iM\alpha} d_{M\Omega}^{(J)}(\beta) e^{-i\Omega\gamma},$$

the angles α and γ represent azimuthal rotations about the polarization vector and the internuclear axis and therefore involve only phase factors. From Eq. (7) one obtains

$$S_{p_1'p_2'p_2p_1}^{q_1'q_2'q_2q_1}(\zeta; \beta) = \sum_{\substack{j' \\ p_1'p_2'}} \sum_{\substack{\ell' \\ \ell' \\ k'k'}} \sum_{\substack{m \\ m'}} \sum_{\substack{n \\ n'}} (-1)^{\phi} (2\ell'+1)(2\ell'+1) d_{-m-n}^{(\ell')}(\beta) (2k+1)(2k'+1) \begin{pmatrix} 1 & 1 & k' \\ p_1' & p_2' & -P' \end{pmatrix} \\ \times \begin{pmatrix} k & 1 & 1 \\ -P & p_2 & p_1 \end{pmatrix} \begin{pmatrix} 1 & 1 & k' \\ q_1' & q_2' & -Q' \end{pmatrix} \begin{pmatrix} k & 1 & 1 \\ -Q & q_2 & q_1 \end{pmatrix} (2J_g+1)(2J_e+1) \begin{pmatrix} J_g & k' & j' \\ M_g & -P' & -M_g+P' \end{pmatrix} \\ \times \begin{pmatrix} J_g & k' & j' \\ \Omega_g & -Q' & -\Omega_g+Q' \end{pmatrix} \begin{pmatrix} k & J_g & j \\ -P & -M_g & P+M_g \end{pmatrix} \begin{pmatrix} k & J_g & j \\ -Q & -\Omega_g & Q+\Omega_g \end{pmatrix} (2j'+1)(2j'+1) \\ \times \begin{pmatrix} j' & J_e & \ell' \\ M_g-P' & -M_e & m' \end{pmatrix} \begin{pmatrix} j' & J_e & \ell' \\ \Omega_g-Q' & -\Omega_e & n' \end{pmatrix} \begin{pmatrix} J_e & j & \ell \\ M_e & -P-M_g & m \end{pmatrix} \begin{pmatrix} J_e & j & \ell \\ \Omega_e & -Q-\Omega_g & n \end{pmatrix} \\ \times \left(\frac{1}{4\pi^2} \int_{\alpha=0}^{2\pi} d\alpha \int_{\alpha'=0}^{2\pi} d\alpha' e^{-i(m\alpha+m'\alpha')} \right) \left(\frac{1}{4\pi^2} \int_{\gamma=0}^{2\pi} d\gamma \int_{\gamma'=0}^{2\pi} d\gamma' e^{-i(\alpha\gamma+\alpha'\gamma')} \right) \\ \times \left(\frac{1}{2} \int_{\beta'=0}^{\pi} \sin \beta' d\beta' d_{-m'-n'}^{(\ell')}(\beta') \right), \quad (8)$$

where $\phi = P + M_e - M_g - Q - \Omega_e + \Omega_g + m + m' - n - n'$ is a phase factor. In Eq. (8) we have set $P = p_1 + p_2$, $P' = p_1' + p_2'$, $Q = q_1 + q_2$ and $Q' = q_1' + q_2'$. The tensor $S_{p_1'p_2'p_2p_1}^{q_1'q_2'q_2q_1}(\zeta; \beta)$ stands for the rotational matrix element associated to a short laser pulse since, under such circumstances, the averaging over the angle β is absent.

In the gas phase all ground-state orientations are equally

probable, however, for a short laser pulse these orientations do not induce the same occupation probability for the resonant state since angular momentum conservation is imposed and the excitation process is not isotropic. In fact, if the laser pulse is short the anisotropic interaction of the electric field vector of the radiation with the molecular polarizability is enhanced. Therefore a selection through the symmetries of the involved states and the polarized incident radiations is

expected to take place and only one class of ground-state orientations can be privileged. In Eq. (8) the last integral is an average over all potential orientations for the internuclear axis in the resonant state and is seen to be nonvanishing only if $\ell' = m' = n' = 0$. Besides, for a diatomic or symmetric-top molecule the azimuthal angles α and γ are redundant and they have to be summed, this results to the condition $m = n = 0$. Then the following selection rules are derived:

$$P = M_e - M_g = \Delta M = -P', \quad (9)$$

$$Q = \Omega_e - \Omega_g = \Delta \Omega = -Q',$$

From the above selection rules and the involved $3-j$ symbols it follows that only the $j' = J_e$ term is allowed to take place. On the other hand, from the sum over all resonant levels j' one observes that these angular momenta have the same projection as J_e both in the LFF and MFF. Then one obtains

$$\mathcal{S}_{p'_1 p'_2 p_2 p_1}^{q'_1 q'_2 q_2 q_1}(\zeta; \beta) = \sum_L (\mathcal{S}_{p'_1 p'_2 p_2 p_1}^{q'_1 q'_2 q_2 q_1}(\zeta))_L^{\Delta J} P_L(\cos \beta), \quad (10)$$

where

$$\begin{aligned} (\mathcal{S}_{p'_1 p'_2 p_2 p_1}^{q'_1 q'_2 q_2 q_1}(\zeta))_L^{\Delta J} &= \sum_{J'_e} \left\{ \sum_{kk'} \sigma_P^{k'k}(p'_1 p'_2 p_2 p_1) \right. \\ &\quad \times \tilde{\sigma}_{\Delta\Omega}^{k'k}(q'_1 q'_2 q_2 q_1) (\Theta_P^{k'k}(J_g M_g; J'_e M_e))_L^{\Delta J} \\ &\quad \left. \times (\tilde{\Theta}_{\Delta\Omega}^{k'k}(J_g \Omega_g; J'_e \Omega_e))_L^{\Delta J} \right\}. \quad (11) \end{aligned}$$

The same tensors appear, both, in the LFF and MFF. We have

$$\sigma_P^{k'k}(p'_1 p'_2 p_2 p_1) = [k][k'] \begin{pmatrix} 1 & 1 & k' \\ p'_1 & p'_2 & P \end{pmatrix} \begin{pmatrix} k & 1 & 1 \\ -P & p_2 & p_1 \end{pmatrix}, \quad (12)$$

and

$$\begin{aligned} &(\Theta_P^{k'k}(J_g M_g; J'_e M_e))_L^{\Delta J} \\ &= [L][J_e][J'_e] \begin{pmatrix} J_e & 0 & J_e \\ M_e & 0 & -M_e \end{pmatrix} \\ &\quad \times \begin{pmatrix} J'_e & L & J_e \\ M_e & 0 & -M_e \end{pmatrix} \Theta_P^{k'k}(J_g M_g; J'_e M_e), \quad (13) \end{aligned}$$

where

$$\begin{aligned} \Theta_P^{k'k}(J_g M_g; J'_e M_e) &= [J_g][J_e] \begin{pmatrix} J_g & k' & J_e \\ -M_g & -P & M_e \end{pmatrix} \\ &\quad \times \begin{pmatrix} J'_e & k & J_g \\ -M_e & P & M_g \end{pmatrix} \quad (14) \end{aligned}$$

is the LFF part of the rotational line factor. Respecting this symmetry, similar expressions are written for the MFF tensors $\tilde{\sigma}_{\Delta\Omega}^{k'k}(q'_1 q'_2 q_2 q_1)$ and $(\tilde{\Theta}_{\Delta\Omega}^{k'k}(J_g \Omega_g; J'_e \Omega_e))_L^{\Delta J}$. For simplicity we have set $[j] = \sqrt{2j+1}$ and $\Delta J = J_e - J_g$.

The term $J'_e = J_e$ of Eq. (11) (or $\Delta J' = J'_e - J_g = \Delta J$) implies that only rotational lines belonging to the rotational branch ΔJ are involved. The remaining terms $J'_e \neq J_e$ (or $\Delta J' \neq \Delta J$) give contributions from lines belonging to adjacent rotational branches which may overlap in energy. Therefore, in general, also terms with $J'_e \neq J_e$ may contribute to the angular distribution if their spectral position overlaps with the bandwidth of the laser pulse. However, it is worth remarking that the levels $J'_e \neq J_e$ will contribute only if $M'_e = M_e$ and $\Omega'_e = \Omega_e$.

For short laser pulses only the degenerated rotational states have to be taken into account whereas the averaging over the internuclear axis orientation is absent. Therefore, the internuclear axis angular distribution of the molecular susceptibility $\chi_{p'_1 p'_2 p_2 p_1}^{(3)}(\beta)$ has to be determined from

$$\chi_{p'_1 p'_2 p_2 p_1}^{(3)} = \frac{1}{2} \int_{\beta=0}^{\pi} \sin \beta d\beta \chi_{p'_1 p'_2 p_2 p_1}^{(3)}(\beta). \quad (15)$$

Finally, we find

$$\begin{aligned} \chi_{p'_1 p'_2 p_2 p_1}^{(3)}(\beta) &= \sum_L \left\{ \sum_{kk'} \sigma_P^{k'k}(p'_1 p'_2 p_2 p_1) \right. \\ &\quad \left. \times (S_{P, \Delta\Omega}^{k'k})_L \tilde{\chi}_{k'k}^{(3)} \right\} P_L(\cos \beta). \quad (16) \end{aligned}$$

The polarization dependence of the angular distribution is condensed in the LFF tensor $\sigma_P^{k'k}$ and is seen to vanish if $p_1 + p_2 + p'_1 + p'_2 \neq 0$, this ensures the conservation of the photon angular momentum in the LFF. The MFF tensor $\tilde{\sigma}_{\Delta\Omega}^{k'k}$, which possesses a similar form but contains the transitional path dependence, has been introduced in the tensor $\tilde{\chi}_{k'k}^{(3)}$. In fact, since the allowed transitional paths $(q_1 q_2 q'_2 q'_1)$ remain indistinguishable the MFF tensor $\tilde{\chi}_{k'k}^{(3)}$ averages over all degenerated MFF transitional paths [15] which satisfy the selection rule $q_1 + q_2 = -q'_1 - q'_2 = \Delta\Omega$. The involved sum is performed by introducing the reduced matrix element [12] of the MFF electric dipole components. We obtain

$$\begin{aligned} \tilde{\chi}_{k'k}^{(3)} &= \frac{N}{6\hbar} \left(\frac{1}{\omega_{eg} - \omega_2 - \omega_1 - i\Gamma_{eg}} \right) \sum_{\mathcal{J}' \mathcal{J} \mathcal{J}''} (\tilde{\rho}_{\mathcal{J}''}^{(0)}) \\ &\quad - \tilde{\rho}_{ee}^{(0)} \tilde{\alpha}_{\Delta\Lambda}^{(k')*}(\omega'_1 \omega'_2) \tilde{\alpha}_{\Delta\Lambda}^{(k)}(\omega_2 \omega_1) \quad (17) \end{aligned}$$

with

$$\begin{aligned} \tilde{\alpha}_{\Delta\Lambda}^{(k)}(\omega_2 \omega_1) &= (-1)^{L_{\mathcal{J}''} - \Lambda_{\mathcal{J}''}} [k] \begin{pmatrix} L_e & k & L_{\mathcal{J}''} \\ -\Lambda_e & \Delta\Lambda & \Lambda_{\mathcal{J}''} \end{pmatrix} \\ &\quad \times \left\{ \frac{1}{\hbar} \sum_{\mathcal{L}_i} \begin{pmatrix} k & 1 & 1 \\ \mathcal{L}_i & L_{\mathcal{J}''} & L_e \end{pmatrix} \left(\frac{1}{\omega_{i\mathcal{J}''} - \omega_2} + \right. \right. \\ &\quad \left. \left. (-1)^k \frac{1}{\omega_{i\mathcal{J}''} - \omega_1} \right) \langle e L_e \| \tilde{\mu} \| i L_i \rangle \langle i L_i \| \tilde{\mu} \| \mathcal{J} L_{\mathcal{J}''} \rangle \right\}. \quad (18) \end{aligned}$$

All information on the laser-molecule interaction concerning the laser pulse time duration and the consequent resonant rotational structure is contained in the molecular orientation asymmetry (MOA) tensor $(S_{P,\Delta\Omega}^{k'k})_L$. We find

$$(S_{P,\Delta\Omega}^{k'k})_L = \sum_{\text{deg}(\zeta)} \mathcal{Q}(\zeta) (\Theta_P^{k'k}(J_g M_g; J'_e M_e))_L^{\Delta J} \times (\tilde{\Theta}_{\Delta\Omega}^{k'k}(J_g \Omega_g; J'_e \Omega_e))_L^{\Delta J}, \quad (19)$$

where the degenerated rotational structure is determined from

$$\sum_{\text{deg}(\zeta)} = \sum_{J_g} \sum_{\Delta J} \sum_{\Delta J'} \sum_{M_g} \sum_{\Delta M}. \quad (20)$$

The presence of the sums over ΔJ and $\Delta J'$ shows that, in general, distinct rotational branches overlap in energy.

The presence of the fractional population of the rotational state in the MOA tensor implies a normalization constant. This normalization may be performed by considering the case where the whole rotational structure of the lowest vibrational level of the ground electronic state is excited with a laser pulse having a time duration long compared to a simple molecular rotation. Taking into account the thermal distribution of the ground rotational levels we may write

$$\mathcal{Q}(\zeta) = \frac{1}{\mathcal{Q}_0} \exp[-(hc/k_B T) \mathcal{F}(J_g)] \Phi(J_g). \quad (21)$$

$\mathcal{F}(J_g)$ is the corresponding rotational term [12] and $\Phi(J_g)$ is a function describing the intensity distribution in the laser pulse [16]. The remaining letters have their usual meaning. Averaging over all internuclear axis orientations and summing over the whole rotational structure we find the vibronic molecular susceptibility to be given by

$$(\chi_{p'_1 p'_2 p_2 p_1}^{(3)})_{ev} = \sum_k \frac{1}{2k+1} \sigma_P^{kk}(p'_1 p'_2 p_2 p_1) \tilde{\chi}_{kk}^{(3)}. \quad (22)$$

The partition function \mathcal{Q}_0 of the thermal distribution is found to be $\mathcal{Q}_0 = \sum_{J_g} (2J_g + 1) \exp[-(hc/k_B T) \mathcal{F}(J_g)] \Phi(J_g)$

Equation (16) is general and holds for any nonlinear process provided that a Raman- or two-photon absorption-type intermediate resonance is present. It is worth remarking that the frequency dependence of the molecular susceptibility factorizes into a global factor for all cases except the singular case $P = \Delta\Omega = \Delta J = 0$, however this singular case is without interest for the steric effect since only alignment may be present. This may be seen from Eq. (18); far from one-photon resonances the MFF polarizability is described by a symmetric 3×3 matrix with six different real elements. Therefore, the antisymmetric term of the tensor $\tilde{\alpha}_{\Delta\Lambda}^{(k)}(\omega_2, \omega_1)$ vanishes and only the $k=0$ and $k=2$ values are allowed. However, the isotropic term $k=0$ is present only if $P = \Delta\Omega = \Delta J = 0$ and, excepting this singular case, only the tensor component $\tilde{\chi}_{22}^{(3)}$ has to be considered. Thus one obtains

$$\chi_{p'_1 p'_2 p_2 p_1}^{(3)}(\beta) = \chi_{p'_1 p'_2 p_2 p_1}^{(3)} \left\{ 1 + \sum_{L=1}^4 (S_{P,\Delta\Omega}^{22})_{L/0} P_L(\cos \beta) \right\}, \quad (23)$$

with $\chi_{p'_1 p'_2 p_2 p_1}^{(3)} = \sigma_P^{22}(p'_1 p'_2 p_2 p_1) (S_{P,\Delta\Omega}^{22})_0 \tilde{\chi}_{22}^{(3)}$, the molecular susceptibility for long laser pulses and, $(S_{P,\Delta\Omega}^{22})_{L/0} = (S_{P,\Delta\Omega}^{22})_L / (S_{P,\Delta\Omega}^{22})_0$, the molecular orientation asymmetry parameter (MOAP). Therefore, the tensor $\tilde{\chi}_{22}^{(3)}$ may be seen as the vibronic susceptibility obtained from unpolarized incident radiations and long laser pulses.

Particular attention has to be taken however for the summation over $\text{deg}(\zeta)$ since the involved degenerated rotational states depend on the specificities of the molecular system, the laser pulse spectral resolution and the temperature of the gas medium.

III. THERMAL DISTRIBUTION OF THE INITIAL STATES AND PARTICULAR CASES

Fourier analysis shows that a wave packet of size $\Delta\mathcal{L}$ contains a spread of wave numbers $\sim 1/\Delta\mathcal{L}$. Consider a laser pulse with a time duration τ_{LP} and spectral resolution ω_{LP} . The intrinsic uncertainty in the behavior of the photons of the laser pulse is built into the wavelike character of propagation; if we wish to be sure that the photon is confined to a region $\Delta\mathcal{L}$ then we must suppose its associated de Broglie wave is squashed into this region. Such a packet cannot, however, be built out of waves of just one wavelength and thus τ_{LP} and ω_{LP} are interrelated by the Heisenberg's uncertainty. If τ_{LP} is measured in picoseconds and the spectral resolution ω_{LP} in cm^{-1} , close to the Fourier limit, the uncertainty principle gives

$$\omega_{LP}[\text{cm}^{-1}] \sim \frac{100}{3} \frac{1}{\tau_{LP}[\text{ps}]}. \quad (24)$$

For a thermal distribution of the initial rotational levels and a short laser pulse multiple rotational levels are expected to participate, however, the major contribution will come predominantly from levels found in the neighborhood of the rotational level $J_g^{\text{max}} = J_g(N_{\text{max}})$ with the maximum population. Under these circumstances, for a specific molecular system the anisotropic interaction depends not only on the characteristics of the laser pulse but equally well on the temperature of the molecular gas. A steric effect for the internuclear axis is expected to take place as long as $\bar{\omega}_{\text{rot}}/\omega_{LP} \ll 1$ with $\bar{\omega}_{\text{rot}}$ the rotational frequency of the level J_g^{max} .

It is interesting to introduce a coefficient indicating the potential degree of the steric effect contained in the laser pulse. Without significant loss of generality we may assume a rigid rotator. The frequency of molecular rotation for a rigid rotator occupying the rotational level J_g is given by $\omega_{\text{rot}}[\text{cm}^{-1}] = 2B_e \sqrt{J_g(J_g + 1)}$ with B_e the rotational constant measured in cm^{-1} . Then the above mentioned laser pulse condition may be introduced by using the ratio $\Omega(T) = \bar{\omega}_{\text{rot}}/\omega_{LP}$. In fact, for a specific molecular system the rotational level J_g^{max} depends exclusively on the temperature [17] T and we have $J_g^{\text{max}} = \sqrt{k_B T / 2B_e h c} - 1/2$. The above ratio then leads into

$$\Omega(T) = \left(\frac{T - T_0}{T_1 - T_0} \right)^{1/2}, \quad (25)$$

with

$$T_0 = \frac{1}{2} \frac{hc}{k_B} B_e, \quad T_1 = T_0 \left(1 + \left(\frac{\omega_{LP}}{B_e} \right)^2 \right). \quad (26)$$

The temperature T_0 , for which $\Omega(T_0)=0$, is a limiting situation where for any $T < T_0$ the lowest rotational level is predominantly populated. Therefore, complex values of this ratio indicate that the rigid rotator does not rotate. For instance, for the CO molecule we find $T_0 \approx 1.38$ K and, at this temperature, already 95% of the molecules occupy the $J_g=0$ level. This specific temperature is defined from the rotational constant exclusively.

For temperatures $T > T_1$ the laser pulse condition exceeds unity and the observed steric effect is expected to be negligible. For this specific temperature the laser pulse time duration and the time of a simple molecular rotation have equal importance. It is seen that this temperature depends both on the specificity of the molecular system as well as on the spectral resolution of the laser pulse, i.e., for the CO molecule and a picosecond laser pulse having a spectral resolution of ~ 30 cm⁻¹ we find $T_1 \approx 335$ K.

Since strong steric effects are expected when $\Omega(T)$ is small compared to unity we define the steric degree of the laser pulse by

$$\sigma_{LP}(T) = 1 - \Omega(T). \quad (27)$$

$\sigma_{LP}(T)$ describes the potential degree of the laser pulse to induce a steric effect in the resonant state. By this we mean that if $\sigma_{LP}(T)$ is small compared to unity the anisotropy of the interaction ‘laser molecule’ is hidden by the isotropy of the initial state, i.e., this is the case for temperatures $T \sim T_1$ where the interacting photon angular momentum is no longer important compared to J_g^{\max} .

For a thermal distribution of the ground rotational levels in absence of external fields the magnetic levels are always degenerated. The MOA tensor given in Eq. (19) becomes

$$\begin{aligned} (S_{P,\Delta\Omega}^{k'k})_L &= \frac{1}{Q_0} \sum_{J_g} \sum_{\Delta J} \sum_{J'_e} [L][J_g][J'_e] \exp[-(hc/k_B T)] \\ &\quad \times \mathcal{F}(J_g) \Phi(J_g) (\mathcal{M}_P^{k'k}(J_g; J'_e))_L^{\Delta J} \\ &\quad \times (\tilde{\Theta}_{\Delta\Omega}^{k'k}(J_g \Omega_g; J'_e \Omega_e))_L^{\Delta J}, \end{aligned} \quad (28)$$

with

$$\begin{aligned} (\mathcal{M}_P^{k'k}(J_g; J'_e))_L^{\Delta J} &= (2k+1)(2J_e+1) \begin{pmatrix} k & 0 & k \\ P & 0 & -P \end{pmatrix} \\ &\quad \times \begin{pmatrix} k & L & k' \\ P & 0 & -P \end{pmatrix} \begin{Bmatrix} k' & L & k \\ J_g & J'_e & k \\ J_e & J_e & 0 \end{Bmatrix}. \end{aligned} \quad (29)$$

The angular distribution is then determined from the general expression given in Eq. (16).

A. Resonance with an isolated rotational branch

The importance of the different terms in the summation over $\text{deg}(\zeta)$ is relevant if one considers the internuclear axis angular distribution for a rotational branch which is well separated in energy. For instance, in the S branch ($\Delta J = \Delta J' = 2$) of the CO $A^1\Pi \leftarrow X^1\Sigma^+$ two-photon electronic transition [18,19] the first 15 rotational lines occupy a spectral region of about 30 cm⁻¹. Therefore two-photon resonance with this branch may be achieved with a laser pulse having a time duration of about $\tau_{LP} \approx 1$ ps, close to the Fourier limit. If T_{CO} is the period of molecular rotation we find for the ratio T_{CO}/τ_{LP} the value of $\sim 10/\sqrt{J_g(J_g+1)}$. Although this ratio remains smaller than unity only for the very first rotational levels the contribution of higher levels becomes rapidly negligible with decreasing temperature. For instance, at 50 K we may see that levels with $J_g > 5$ give a minor contribution since the corresponding population is small. Therefore, even for this temperature the steric effect may be significant; the corresponding steric degree of the laser pulse is found to be $\sigma_{LP} \approx 0.62$. For $T = 10$ K only the levels $J_g = 0, 1, 2$ contribute and $\sigma_{LP} \approx 0.84$ whereas for $T < T_0$ all molecules occupy the $J_g = 0$ level and thus $\sigma_{LP} = 1$. Under the above circumstances the sum over $\text{deg}(\zeta)$ is reduced into a restricted number of ground rotational levels depending upon the temperature and the spectral resolution of the laser pulse. Since for the above transition $\Delta\Lambda \neq 0$ the angular distribution is obtained from Eq. (23) and the MOA tensor is obtained from Eq. (28) by considering only the term $\Delta J = \Delta J' = J_e - J_g$.

In Figs. 1(a)–1(d) we considered a nonlinear process in the CO molecule involving a two-photon resonance with the S branch of the $A^1\Pi \leftarrow X^1\Sigma^+$ electronic transition. However, the obtained results will hold equally well for the $N_2[a^1\Pi_g \leftarrow X^1\Sigma_g^+]$ two-photon resonance since the S branch is also well separated in energy [19] and the involved rotational constant is roughly the same as that of the CO molecule. In Fig. 1(a) we have drawn [20] the internuclear axis angular distribution for $T = 10$ K and for polarized laser beams having $P = p_1 + p_2 = \Delta\Omega$. We may see in this figure that the contributions from the populated rotational levels are always constructive and as a result the angular distribution of the S branch is enhanced. However, with increasing temperature the angular momentum of the participating rotational levels becomes important and the steric effect decreases. The above distribution shows that the excitation probability is particularly enhanced if the internuclear axis is collinear to the laboratory quantization axis. In fact, classically, this is the only orientation in space for the internuclear axis where, both, the LFF and MFF components of the photon angular momentum k are found to be equal ($P = \Delta\Omega$).

For lower temperatures the $J_g = 0$ level is more and more populated and we reach a limiting situation where the angular distribution becomes insensitive in temperature. This takes place for $T < T_0$ and, if $P = \Delta\Omega$, the class of molecules whose internuclear axis is anticollinear to the quantization axis during the short excitation time interval cannot be excited at all. The above probability is enhanced for two privileged orientations, namely, for $\beta_0 = 0$ and $\beta_1 = 105^\circ$ (or for $\beta_0 = 0$ and $\beta_1' = -105^\circ$) in the plane defined from the two crossed laser beams. In fact, for obtaining $P = \Delta\Omega = 1$, the

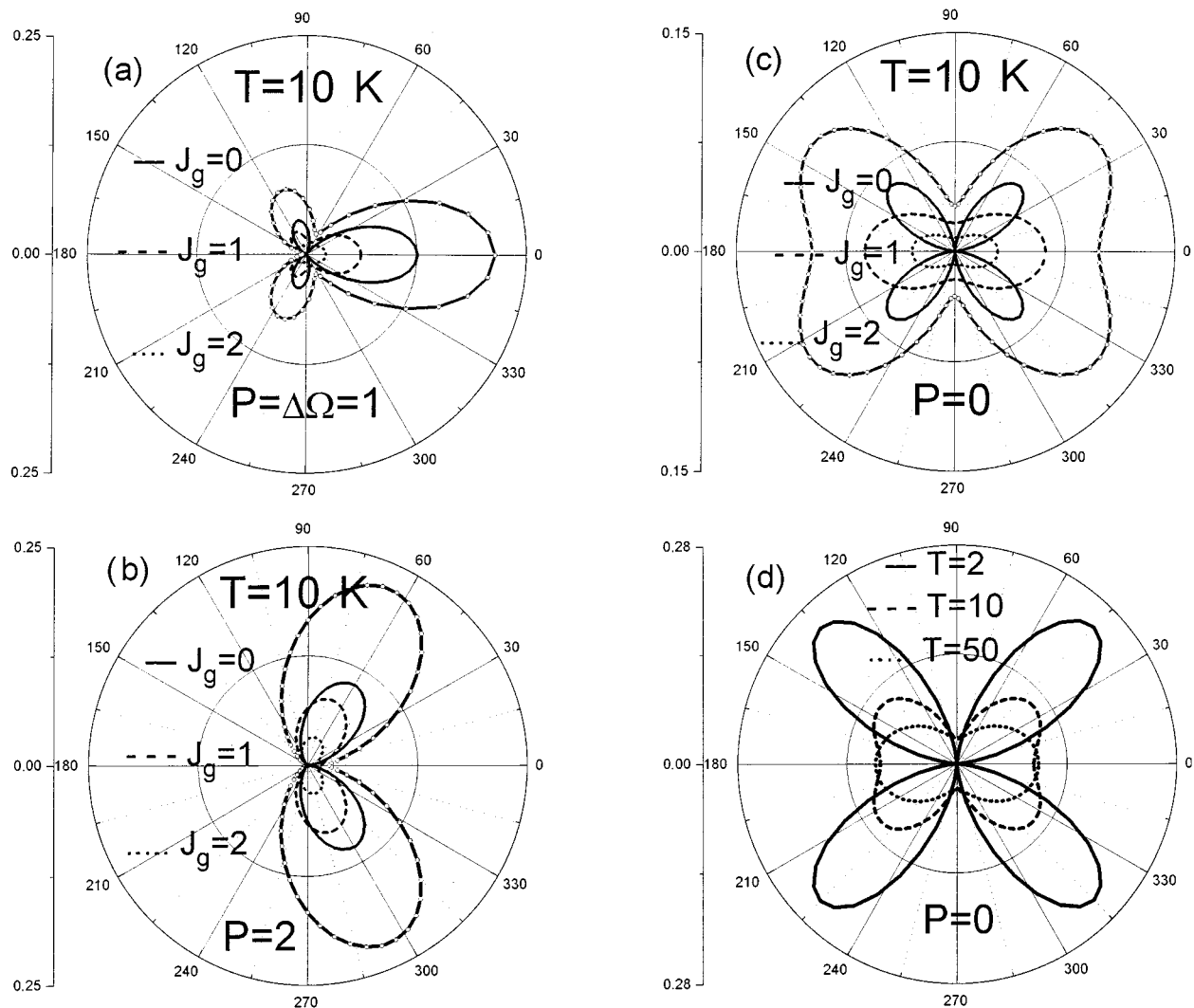


FIG. 1. The steric effect induced in the molecular susceptibility (arbitrary units) from the presence of a two-photon intermediate resonance and a short laser pulse. The intermediate resonance (here ${}^1\Pi \leftarrow {}^1\Sigma$) may be two-photon absorption- or Raman-type resonance. The broad spectral bandwidth of the short laser pulse excites all the rotational levels of the S branch and the angular distribution (drawn versus the angle β which defines the internuclear axis orientation in the laboratory frame) is shown by $\circ-\circ-\circ-\circ$. In all cases we have $p_1' = -p_1$ and $p_2' = -p_2$. (a) The condition $P = \Delta\Omega \neq 0$ implies strong steric effects for the internuclear axis orientation. Here we assumed a thermal distribution for the initial rotational levels and we observe that the steric effect is enhanced for low temperatures since the contributions from the excited rotational levels are constructive. With the choice of the polarizations p_1 and p_2 we may excite selectively the class of molecules whose internuclear axis is collinear ($P = p_1 + p_2 = \Delta\Omega$) or anticollinear ($P = -\Delta\Omega$) to the laboratory quantization axis. Then the excited molecules will rotate in phase and find repeatedly the same orientation in space. (b) If $P \neq \Delta\Omega$ (with $P \neq 0$) only the plane of molecular rotation contains a net helicity. Here $P = 2$ and the excited molecules are constrained to rotate about the laser beam direction. This helicity occurs from contributions of the very first rotational levels and thus cease to be visible with increasing temperature. From (a) and (b) we may extract information on the polarization intensity ratio $\chi_{000}^{(3)}(\beta)/\chi_{-1-11}^{(3)}(\beta)$. For $T = 10$ K we find, 8.73, 1, $1/8.73$, and 0.35 for $\beta = 0, \pi/6, \pi/3$, and $\pi/2$, respectively. (c) With $P = 0$ (here $p_1 = p_2 = 0$), both, the internuclear axis steric effect and the helicity of the plane of rotation are absent. However, we may have a distinct alignment for each participating rotational level. If this is the case the overall alignment will possess a strong dependence on the gas temperature (if $P = 0$ with $p_1 = -p_2 = 1$ the above scale must be divided by 4). From (a), (b), and (c) we may verify that for $\beta = \beta^* = \pi/6$ we have $\chi_{000}^{(3)}(\beta^*) = \chi_{-1-11}^{(3)}(\beta^*) = \chi_{-111}^{(3)}(\beta^*)$, this specific angle varies slowly with temperature. (d) The alignment (here $p_1 = p_2 = p_2' = p_1' = 0$) induced in an excited state may depend drastically on temperature. Since the angular distribution obtained from the spherically symmetric ground rotational state ${}^1\Sigma(J_g = 0)$ differs from that obtained from a ${}^1\Sigma(J_g \neq 0)$ state, their relative contribution in the angular distribution implies a radical change in the alignment when the temperature increases from T_0 to T_1 (see text for the definition of T_0 and T_1). For $p_1 = -p_2 = p_2' = -p_1' = 1$ the above scale must be divided by 4, whereas for $p_1 = p_2 = 0$ and $p_1' = -p_2' = 1$ it is divided by 2.

first laser beam must be right circularly polarized whose direction defines the laboratory quantization axis, then the second laser beam is linearly polarized with the polarization vector found along the same quantization axis. Since the lin-

early polarized radiation may be seen as a superposition of two circularly polarized right and left radiations and the angular momentum of the excited molecule is exclusively the absorbed photon angular momentum this momentum may be

lying either between β_0 and β_1 or between β_0 and β'_1 . The orientation probability for β_0 being predominantly enhanced, roughly, only molecules collinear to the quantization axis are excited. Then, following excitation, the excited molecules will be constrained to rotate in phase about the absorbed photon angular momentum by finding repeatedly the orientation of the laboratory of the quantization axis. It is worth remarking that the alignment or orientation communicated to the molecular excited state cannot be lost by simple molecular rotation.

If $P \neq \Delta\Omega$ the steric effect decreases drastically. This is shown in Fig. 1(b) where the angular distribution is drawn for $P=2$. At $T=10$ K, the different contributions due to the $J_g=0,1$, and 2 rotational levels are shown and we observe that the steric effect decreases with J_g since in this case the photon angular momentum becomes less and less important. Therefore at ambient temperatures only a weak alignment is expected to take place.

If $P=0$ only alignment may take place, however, this alignment may depend dramatically on the temperature. We observe in Fig. 1(c) that the angular distribution of the $J_g=0$ level differs radically from the angular distribution of the remaining rotational levels. In fact only the ground rotational level is spherically symmetric and this difference implies a drastic dependence on the temperature. The temperature dependence in the angular distribution of the S branch has been drawn in Fig. 1(d); for temperatures lower than $\sim T_0$ the angular distribution becomes insensitive to the temperature since only the contribution of the ground rotational level is important. This is also the case for $T > T_1$ where the contribution of the ground rotational level is now without effect, however, the alignment is quite different.

B. A prepared initial rotational state and the involved M channels

If the initial state is well prepared in some vibrational level $v_g \neq 0$ where only one rotational level is populated we obtain

$$\chi_{p'_1 p'_2 p_2 p_1}^{(3)}(J_g; \beta) = (2J_e + 1) \sum_{M_g M_e} \chi_{p'_1 p'_2 p_2 p_1}^{(3)} \times (J_g M_g; J_e M_e) (d_{M_e \Omega_e}^{(J_e)}(\beta))^2, \quad (30)$$

with

$$\begin{aligned} \chi_{p'_1 p'_2 p_2 p_1}^{(3)}(J_g M_g; J_e M_e) \\ = \sum_{k'k} \sigma_P^{k'k}(p'_1 p'_2 p_2 p_1) \Theta_P^{k'k}(J_g M_g; J_e M_e) \tilde{\Theta}_{\Delta\Omega}^{k'k} \\ \times (J_g \Omega_g; J_e \Omega_e) \tilde{\chi}_{k'k}^{(3)}. \end{aligned} \quad (31)$$

The angular distribution of the rotational line $J_g \rightarrow J_e$ is formed from contributions due to the $2M_g + 1$ independent channels. However each M channel possesses a distinct occupation probability since the symmetry of the electronic states in conjunction with the polarization of the incident photons have the effect of selecting those molecular orientations where the transfer of the angular momentum is easiest.

For short laser pulses this asymmetry leads to the steric effect; i.e., the occupation probability of the channel $M_g = \Omega_e - P$ is particularly enhanced for $\beta=0$ whereas, for this orientation, the occupation probability of any other channel vanishes. In fact, for this specific channel we have $M_e = \Omega_e$ and the reduced rotation matrix element $d_{M_e \Omega_e}^{(J_e)}(\beta)$, as expected, is enhanced for $\beta=0$. Classically, this is the only orientation in space where the total angular momentum of the molecule presents a common projection both in the LFF and MFF quantization axes. This has been drawn in Fig. 2(a) for the $CO[A^1\Pi(v_e, J_e=4) \leftarrow X^1\Sigma^+(v_g \neq 0, J_g=2)]$ electronic resonance [21]; we observe that the steric effect in the S branch of the $^1\Pi \leftarrow ^1\Sigma$ electronic resonance finds its origin to the enhancement of the occupation probability of the $M_g=0$ ($M_e=\Omega_e$) channel. For this channel the steric effect is singular, moreover, it becomes sharper and sharper with increasing J_g . In practice, however, with increasing J_g the steric effect is limited since for increasing molecular rotation the steric degree of the laser pulse becomes less and less important. For instance, excitation of the $S(J_g=1)$ line with a picosecond laser involves a steric degree $\sigma_{LP}(J_g=1) \sim 0.83$ whereas for the $J_g=4$ level we have $\sigma_{LP}(J_g=4) \sim 0.46$. Therefore for high rotational levels shorter and shorter laser pulses are required. However, the corresponding spectral bandwidth increases and rotational lines belonging to adjacent rotational branches may also contribute. Finally it should be noted that in the case where the initial state is the lowest rotational level the steric degree of the laser pulse equals always to unity.

In particular, the internuclear axis angular distribution in the resonant electronic state is found to be singularly simple if the molecule is found initially in a $^1\Sigma(J_g=0)$ -state. We find

$$\begin{aligned} \chi_{p'_1 p'_2 p_2 p_1}^{(3)}(0; \beta) \\ = \delta_{J_e, 2} \delta_{M_e, P} \sigma_P^{22}(p'_1 p'_2 p_2 p_1) (d_{P \Delta\Omega}^{(J_e)}(\beta))^2 \tilde{\chi}_{22}^{(3)}. \end{aligned} \quad (32)$$

This holds equally well for the ground vibrational level provided that the temperature is lower than the temperature T_0 . The above distribution is a limiting situation for the angular distribution since the degree of orientation or alignment cannot be improved. We observe that the polarization $P=p_1+p_2$ populates exclusively the rotational state $|J_e \Omega_e M_e\rangle = |2\Delta\Omega P\rangle$. Furthermore, each state possesses a distinct angular distribution and we observe a sharper steric effect for $P=\Delta\Omega$ (or $M_e=\Omega_e$) where the internuclear axis is collinear to the polarization vector. This is explained by the fact that the angular momentum of the excited rotational state is exclusively the photon angular momentum state $|2\Delta\Omega P\rangle$, therefore we may have a common projection in the LFF and MFF quantization axes only if the internuclear axis is collinear to the laboratory quantization axis. On the other hand, if $P=-\Omega_e$ the internuclear axis must be anticollinear.

More specifically, in Fig. 2(b) we have drawn the angular distribution of the $|J_e \Omega_e M_e\rangle = |2M_e\rangle$ states involved in the electronic transition $^1\Delta_g \leftarrow ^1\Sigma_g$ which is two photon allowed. This may be the case of $O_2[a^1\Delta_g \leftarrow b^1\Sigma_g^+]$ or

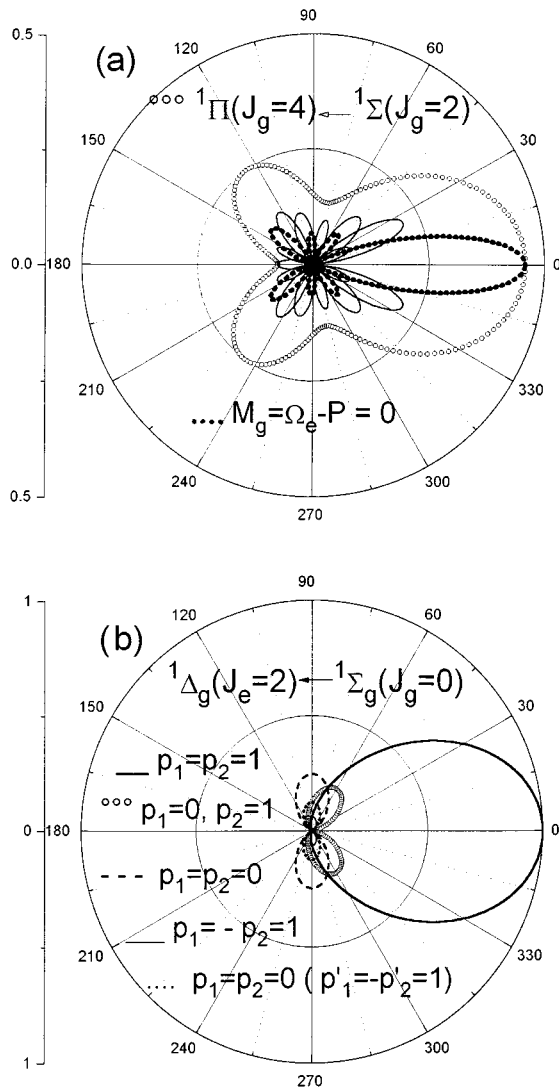


FIG. 2. From the angular distribution information on the β -dependent polarization intensity ratio may be extracted. Furthermore, from a prepared initial rotational state the relative occupation probability of the involved M channels and their angular distribution may be probed. (a) The steric effect in a rotational line is due to the enhancement of the occupation probability of the $M_e = \Omega_e$ (or $M_e = -\Omega_e$) channel since this is the only channel for which the occupation probability in the $\beta=0$ (or $\beta=\pi$) direction is nonvanishing. This enhancement takes place, however, only if the condition $P=\Delta\Omega$ (or $P=-\Delta\Omega$) is present. It is the relation between the parameters P and $\Delta\Omega$ that modifies the relative occupation probability of the M channels. (b) In the limiting situation where the prepared initial state is the state $1\Sigma(J_g=0)$ only the $M_e=P$ channel is occupied since $M_g = \Omega_g = 0$. The angular momentum in the resonant rotational state is exclusively the photon angular momentum state and this allows one to select internuclear axis orientations by exciting the appropriate M channel. The shape of the angular distribution, as well as the amplitude, depend on the particular value of P and thus, for a short laser pulse, the polarization intensity ratio depends on β . However, for polarizations with $P=0$ the above ratio becomes independent of β ; we find $\chi_{-11-11}^{(3)}/\chi_{0000}^{(3)}=1/4$ and $\chi_{00-11}^{(3)}/\chi_{0000}^{(3)}=\chi_{-1100}^{(3)}/\chi_{0000}^{(3)}=1/2$, and this, independently of the time duration of the laser pulse.

$H_2[J^1\Delta_g \leftarrow X^1\Sigma_g^+]$. For these particular cases only one rotational line is present since $J_g=0$ and $\Omega_e=2$, moreover, due to angular momentum conservation, only one M channel may be occupied if the photons polarization is specified.

IV. CONCLUDING REMARKS

In this work we have determined the internuclear axis steric effect induced in a diatomic or symmetric-top molecule when a short laser pulse is involved. Steric selection rules have been derived and the influence of the gas temperature on the spatial arrangement of the excited molecules has been investigated. In particular, we have shown that when more than one rotational state is excited simultaneously contributions from these states may be constructive and result in the enhancement of the steric effect. For a physical insight of the steric effect it may be instructive to attempt an intuitive description for the interacting system.

During the short interaction time of the laser pulse with the molecular system the projection of the photon angular momentum k on the LFF and MFF quantization axes is given, respectively, by P and $\Delta\Omega$. The condition $P=\Delta\Omega$ is expected to take place only if these axes present a common orientation in space; if this is the case, however, for any ground rotational level J_g we must have $M_g = \Omega_g$, i.e., in Fig. 2(a) we see that for the $A^1\Pi \leftarrow X^1\Sigma^+$ resonance the $M_g=0$ channel is singularly enhanced for $\beta=0$ if $P=\Delta\Omega$. Since for any rotational line the quantity $P=M_e-M_g$ remains a common parameter the above arguments suggest that if the condition $P=\Delta\Omega$ is present we must have separately $M_g = \Omega_g$ and $M_e = \Omega_e$. Furthermore, the two orientations $\Delta\tilde{\Omega}$ and $-\Delta\tilde{\Omega}$ along the laboratory quantization axis contain distinct excitation probabilities if a circularly polarized photon is involved. This distinction leads to a steric selection rule for the orientation of the internuclear axis since for the conservation of energy and angular momentum any orientation in space cannot have equal importance.

In fact, for a diatomic molecule the angular momentum is associated with electronic motion and can be treated as part of the electronic energy which has been separated off. If ϕ is the azimuthal angle for the position of the electron and $\tilde{\mathcal{L}}_z$ the projection of its orbital angular momentum along the molecular axis the rate of change of the expectation value of $\tilde{\mathcal{L}}_z$ may be approximated by $d\langle\tilde{\mathcal{L}}_z\rangle/dt \approx -\langle\partial\mathcal{V}/\partial\phi\rangle$; conservation of the orbital angular momentum then implies that the potential energy \mathcal{V} of the moving electron must remain independent of ϕ . Consider a right circularly polarized photon for which the angular momentum is well defined in the laser beam direction; the rotating polarization vector of the incident photon will let the potential energy of the electron independent of ϕ only if the molecular axis is aligned with the polarization vector: moreover, the two opposed orientations are associated with different energies for the interacting system since a rotation of π for the molecule is equivalent in changing the sense of rotation of the electron with respect to the rotating polarization vector. For a given rotational branch and polarization only one of the two orientations is allowed. This also explains the opposed angular distribution observed for P and $-P$ when a rotational branch is found in resonance.

If the internuclear axis is well aligned with the polarization vector the transfer of energy and angular momentum may take place without destroying the axial symmetry of the molecular system [22]. Instead, any deviation from this specific configuration implies a ϕ -dependent potential and, in this case, the orbital angular momentum cannot be conserved during the interaction time. It is the broken symmetry that induces a reorientation of the molecular system, since the total angular momentum of the system "electron + molecule" must be conserved; a strong dependence on ϕ contains strong inertial effects if a short laser pulse is involved. Therefore symmetry aspects dictate interaction and, in the underlying dynamics, inertial effects imply that distinct orientations in space contain distinct excitation probabilities; i.e., for $P = \Delta\Omega$ only the $\beta = 0$ orientation is enhanced whereas for $P = -\Delta\Omega$ the $\beta = 0$ value is not allowed to take place at all.

It has been shown that the angular dependence is globally

factorized from the frequency dependence of the nonlinear process, and this, essentially for all cases where the adiabatic approach may be applied. The angular dependence reflects exclusively the symmetry of the involved molecular states and the spatial arrangement of the incident polarizations and covers all third-order nonlinear processes where a two-photon intermediate resonance is present; i.e., the angular dependence is insensitive to whether the two-photon resonance is a two-photon absorption- or Raman-type resonance, only the amplitude of the nonlinear process will be concerned through the electronic-vibrational tensor $\tilde{\chi}_{22}^{(3)}$.

Although the present work has been done for molecular states which are well described by Hund's case a coupling this procedure is general and may be applied to any coupling case sequence by introducing the appropriate wave functions. Moreover, this treatment may be readily extended to higher order molecular susceptibilities, if desired.

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