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Laser-induced deformation of triatomic molecules: Influence on tunnel ionization

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We consider a type of light-dressing effect in molecules which is due to laser-induced deformation of molecules. We derive general formulas which describe the change of the equilibrium bond lengths, bending angles, and vibration frequencies for a polyatomic molecule. Up to the second-order terms in the field strength, the normal coordinates of the molecule are not changed. Explicit expressions for the change of the geometric parameters and vibration frequencies are found for a nonlinear triatomic molecule of the A_2B type. These results are applied to calculation of the tunnel-ionization rates for H_2O, H_2O^+, and SO_2 molecules, both in ac and dc fields. The main influence of the laser-induced deformation on the tunnel ionization is due to the changes in Franck-Condon factors, which are determined by overlap of the nuclei wave function of the molecule and its residual ion. In a laser field with an intensity of $\sim 10^{14}$ W/cm^2, the contribution of the laser-dressing effect to the ionization rate is within 5% for H_2O and H_2O^+, while accounting for this effect changes the ionization rate of the SO_2 molecule by up to 20 times depending on the molecule's orientation with respect to the electric-field vector. Such a large difference is due to the electronic structures of these molecules.

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I. INTRODUCTION

Processes of the interaction of laser radiation with simple molecules have been studied for several decades [1–9]. One of the most important among these processes is the ionization of molecules which, in particular, plays a determining role in the gas filamentation phenomenon which has been under active study in recent years [10–15].

For most of the currently available powerful laser sources, the ionization takes place in the tunnel regime according to Keldysh theory [16]. Developed originally for atoms, this theory was directly generalized for tunnel ionization of molecules in Refs. [17,18] and currently is known as Ammosov-Delone-Krainov theory for molecular orbitals (MO-ADK). Nevertheless, unlike atoms, the ionization of molecules requires substantial modifications of Keldysh theory.

Madsen *et al.* investigated an influence of the molecular dipole moment on their tunnel-ionization rate in a dc electric field. Their basic model (tunnel ionization of a simple molecule with a structureless core) is considered in detail in Ref. [19]. In their further papers, these authors applied this theory to the ionization of linear [20] and nonlinear (e.g., H_2O [21]) molecules, where the overlap between the electron orbitals of the molecular core and the formed ion was accounted for using the Dyson orbital technique [22].

One of the important results of the above-mentioned works is an essential role of the linear Stark effect, which arises in some molecules due to a permanent dipole moment. In Ref. [23], we showed that the permanent dipole moment can be neglected for the multiphoton-ionization regime, but it is important for the tunnel regime. Taking into account the permanent dipole moment, the tunnel-ionization rate calculated in Ref. [23] is changed by as much as ten times for the case of laser radiation linearly polarized along the molecule axis.

Another important difference between molecules and atoms is due to the vibrational degrees of freedom. In fact, the molecular vibrations were not taken into account in Refs. [17,18] where the ionization rate was calculated for the "frozen" nuclei with subsequent averaging over the internuclear separation. Such a method can be considered as a quasiclassical approach. The quantum treatment of the molecular vibrations performed in Refs. [15,24,25] involves Franck-Condon factors (FCFs) which arise in the calculation of molecular oscillator strengths (see, e.g., [26]). In Refs. [15,24,25], an anharmonic Morse oscillator model was used to calculate FCFs for diatomic molecules.

A more adequate quantum treatment of molecular nuclear motion, which allows calculation of the tunnel-ionization rate for vibrationally excited molecules, is the so-called inelastic tunneling model. Developed for atoms in our earlier papers [27–31], this approach has demonstrated a good agreement with experimental results from Refs. [32,33], including the experiment [34] stimulated by our inelastic tunneling theory. In molecules, the inelastic tunneling appears as an anti-Stokes-enhanced tunnel effect. It was demonstrated in Ref. [15] in the calculation of tunnel ionization of a nitrogen molecule, which is important for understanding the kinetics of filamentation in the Earth's atmosphere. Moreover, the anti-Stokes-enhanced tunnel effect can be of interest for laser isotope separation. The corresponding estimations were done for molecular hydrogen [24] and hydrogen halides [25]. A quantum treatment of nuclear motion was also done in Refs. [35–37].

In recent experiment [38] in laser-assisted electron-atom scattering, an important role of the light-dressing effect in atoms was demonstrated with a good agreement with the theoretical model proposed by Zon [39]. The laser-assisted modification of vibrational frequencies and equilibrium internuclear separation of a diatomic molecule (see [40]) can be considered as a similar light-dressed effect in molecules (LDEM). In application to the tunnel ionization, LDEM works via changing FCF values in a laser field. The calculations

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taking into account the LDEM-induced change of vibrational parameters of the H_2 molecule result in a change of its tunnel-ionization probability by two times under the laser-field intensity of $\gtrsim 10^{14}$ W/cm^2 [24].

This research aims to generalize the LDEM theory to polyatomic molecules. To calculate the changes in the vibrational parameters of molecules in the laser field, we apply the method proposed by Kern and Matcha [41] and developed later by Pandey and Santry [42] for nonadiabatic molecular susceptibilities in a dc electric field. The odd-order (in the field strength) contributions to the molecular energy, which arise in the dc field, are absent in the ac field at IR or optical frequencies [43] and this is the main difference between the ac and dc field-induced modification of molecular geometry. Note the nonadiabatic study of the optical properties of the simplest molecules performed in Ref. [44] with a variation method using oscillator wave functions. Reference [45] contains a review of further papers of these authors, for instance, application of the modification of molecular geometry and vibrational spectra (so-called vibrational Stark effect [46]) in studies of the Kerr effect, and electric-field-induced second- and third-harmonic generation.

A brief outline of the present paper is as follows. In Sec. II, we give a brief sketch of Dyson orbitals for polyatomic molecules in the Born-Oppenheimer approximation. Section III contains formulas for the tunnel-ionization rate in a dc electric field and in monochromatic laser radiation. A theoretical description of monochromatic laser-induced modification of geometry and vibrational parameters of a polyatomic molecule is given in Sec. IV. As an example, we consider the deformation of a symmetric nonlinear molecule of the A_2B type. Section V contains the results of numerical calculations for H_2O, H_2O^+, and SO_2 molecules. Some formulas needed for intermediate calculations are given in the Appendices. The transformation from the Cartesian to normal coordinates is given in Appendix A. The explicit formulas accounting for the influence of molecular deformation on FCFs are presented in Appendix B.

The atomic units ($\hbar = m_e = e = 1$) are used hereafter, except in specified cases.

II. DYSON ORBITAL IN POLYATOMIC MOLECULES

The Born-Oppenheimer approximation (BOA) is widely used in the study of interactions between molecules and electromagnetic radiation. However, dissociative ionization and Coulomb explosion are exceptional cases for which BOA does not apply (see, e.g., [47–51]). These cases are not considered in the present paper. For a complete description of the molecular stationary states in the BOA framework, the many-electron wave functions should be multiplied by the wave functions of nuclear vibrational motion,

$$\Psi_{\mu,\{v_\mu\}}(\{\boldsymbol{r}\},\{\boldsymbol{R}\}) = \chi_{\mu,\{v_\mu\}}(\{\boldsymbol{R}\})\Phi_\mu(\{\boldsymbol{r}\};\{\boldsymbol{R}\}). \tag{1}$$

Here, $\mu = i$ denotes the initial state which corresponds to the neutral molecule, while $\mu = f$ denotes the final state which corresponds to its residual ion. The compound subscript $\{v_\mu\}$ stands for all vibrational quantum numbers of the molecule; $\{\boldsymbol{r}\}$ corresponds to all electron coordinates and $\{\boldsymbol{R}\}$ to all nuclear coordinates. The vibrational state of the molecule is given by the χ function, and the electronic state is described by the Φ function which depends parametrically on the nuclear positions, $\{\boldsymbol{R}\}$.

In the traditional ADK and MO-ADK models, the atomic or molecular ionic core is considered to be "frozen", i.e., the core state remains unchanged after the departure of the tunneling electron. However, both the core electron and nuclear motion wave functions in a neutral molecule are generally different from those of the residual ion. To take into account this difference, we use the Dyson orbital which is an overlap between the core configurations of the neutral molecule in the initial state and its ion in the final state. According to Eq. (1), in the single active electron (SAE) approximation, the Dyson orbital is

$$\Psi^{(\mathrm{Dyson})}_{\{v_f v_i\}}(\boldsymbol{r}) = \int \{d^3R\}\, \chi^*_{f,\{v_f\}}(\{\boldsymbol{R}\})\, \chi_{i,\{v_i\}}(\{\boldsymbol{R}\}) \times \int \{d^3r'\}\, \Phi^*_f(\{\boldsymbol{r}'\};\{\boldsymbol{R}\})\Phi_i(\{\boldsymbol{r}'\},\boldsymbol{r};\{\boldsymbol{R}\}). \tag{2}$$

Here, $\boldsymbol{r}$ is the active (tunneling) electron coordinate, while $\{\boldsymbol{r}'\}$ stands for the coordinates of the electrons in the neutral molecule core or in its residual ion. The following notation for the volume elements are used in the integration:

$$\{d^3r'\} \equiv \prod_{i=1}^{N_e} d^3r_i, \quad \{d^3R\} \equiv \prod_{j=1}^{N_a} d^3R_j,$$

where N_e is the number of electrons in the residual molecular ion and N_a is the number of atoms in the molecule.

The first integral in Eq. (2) extends the common Dyson electronic orbital with an additional account for the nuclear degrees of freedom. For small vibration amplitudes, this integral determines the FCF (see below). For the further use of Eq. (2), it should be simplified under the following three assumptions: (i) We take into account the small amplitude of classical vibrations as compared to the equilibrium internuclear separation. (ii) We neglect the change of the orientation (i.e., rotation) of the molecule during the tunneling process. (iii) We use the single-electron (Hartree-Fock) approximation for the electron configuration.

Under the assumptions listed above, Eq. (2) is simplified (for details, see Ref. [25]),

$$\Psi^{(\mathrm{Dyson})}_{\{v_f v_i\}}(\boldsymbol{r}) \approx \mathcal{I}^{(v)}_{fi}\mathcal{I}^{(e)}_{fi}\Psi(\{\boldsymbol{R}_{ei}\},\boldsymbol{r}). \tag{3}$$

Here,

$$\mathcal{I}^{(v)}_{fi} = \int \chi^*_{f,\{v_f\}}(\{\boldsymbol{R}_{ef}\},\{\xi\})\, \chi_{i,\{v_i\}}(\{\boldsymbol{R}_{ei}\},\{\xi\})\{d\xi\} \tag{4}$$

is the overlap between the vibrational wave functions; the structure of this integral will be discussed below. The equlibrium nuclear coordinates $\{\boldsymbol{R}_{ei,ef}\}$ are related to the neutral molecule or its ion, respectively, in their local coordinate frames. The integration is made over the set of internal vibrational coordinates, $\{\xi\}$, with the volume element,

$$\{d\xi\} \equiv \prod_{j=1}^{n} d\xi_j,$$

where $n = 3N_a - \beta$ is the number of vibrational degrees of freedom, and $\beta = 6$ for nonlinear and 5 for linear molecules.

The integral $\mathcal{I}_{fi}^{(e)}$ represents the overlap between the electronic wave functions of the residual molecular ion and those of the neutral molecule core. In the Hartree-Fock approximation, $\mathcal{I}_{fi}^{(e)}$ is reduced to the product of one-electron wave functions, ψ_i, of the neutral molecule and the wave functions, ψ_f, of its residual ion:

$$\int \psi_f^*(\{\boldsymbol{R}_{ef}\},\boldsymbol{r}')\psi_i(\{\boldsymbol{R}_{ei}\},\boldsymbol{r}')\,d^3r'.$$

This integral can be calculated analytically using the Gaussian orbital method (see the Appendix in Ref. [15]). The last multiplier in Eq. (3), $\Psi(\{\boldsymbol{R}_{ei}\},\boldsymbol{r})$, represents the wave function of the tunneling electron. As a rule, this is the highest-occupied molecular orbital (HOMO).

The tunnel-ionization theory requires knowledge of the asymptotic form of the HOMO wave function. For an arbitrary polyatomic molecule, this form is [18]

$$\Psi(\{\boldsymbol{R}_{ei}\},\boldsymbol{r}) \approx \kappa^{3/2}(\kappa r)^{\nu-1}e^{-\kappa r}\sum_{lm} C_{lm}Y_{lm}(\hat{\boldsymbol{r}}), \tag{5}$$

where $\kappa = (2I_{\mathrm{p}})^{1/2}$, I_{p} is the ionization potential of the molecule, $\nu = \kappa^{-1}$ is the effective principal quantum number, $\hat{\boldsymbol{r}} = \boldsymbol{r}/r$, and $\{C_{lm}\}$ is a dimensionless structure HOMO factor accounting for the noncentral potential of the molecular core which influences the active electron's motion.

In linear molecules, the projection of the electron's orbital angular momentum onto the molecular axis m is conserved, so the molecular axis can be chosen as the quantization axis. In this case, the sum in Eq. (5) contains the terms with a fixed m value only. In the case of nonlinear molecules, m is not a good quantum number and terms with different m values will enter in the sum in Eq. (5). It is convenient to choose the quantization axis for the nonlinear molecules so that the maximal number of the C_{lm} coefficients turns to zero. In particular, for symmetric A_2B (or, more exactly, ABA) molecules, the quantization axis can be chosen along the molecule's symmetry axis, which is the bisectrix of the equilibrium bending angle.

III. TUNNEL IONIZATION OF A POLYATOMIC MOLECULE

A theory of tunnel ionization by dc field $\boldsymbol{F}$, proposed for polyatomic molecules in Refs. [18,19], is based on the model of a single active electron bound by a structureless core's field. There exist three types of the many-body effects due to the core structure:

(i) *Overlap between the electron shells of the residual ion and the neutral molecule core.* This effect can be taken into account with the help of the Dyson orbital which has the form of (3) in BOA.

(ii) *Excitation of the internal degrees of freedom of the molecule.* The electron configuration of the residual atomic ion excited due to tunnel ionization can be taken into account by the "inelastic tunneling" model proposed in Ref. [27]. In Ref. [24], this model was adapted for molecules accounting for the excitation and deexcitation of the vibrational degrees of freedom due to tunneling of the active electron.

(iii) *Stark shift.* The bound electrons' energy undergoes a Stark shift under a dc field. For polar molecules, this shift is linear in the electric-field strength F and it can have a strong influence on the tunnel-ionization rate [19,23].

The many-body effects of types (i) and (ii) above are accounted for by the following substitution:

$$I_{\mathrm{p}} \rightarrow I_{\mathrm{p}} + \Delta_{fi}^{(v)} + \Delta_{fi}^{(1)} + \Delta_{fi}^{(2)}. \tag{6}$$

Here,

$$\Delta_{fi}^{(v)} = E_f^{\{v_f\}} - E_f^{\{0\}} - E_i^{\{v_i\}} + E_i^{\{0\}}, \tag{7}$$

where $E_\mu^{\{0\}}$ is the vibrational energy in the ground vibrational state and $E_\mu^{\{v_\mu\}}$ is the vibrational energy in the initial ($\mu = i$) and final ($\mu = f$) states characterized by the set of vibrational quantum numbers, $\{v_\mu\}$. The other quantities entering Eq. (6) have the following meaning:

$$\Delta_{fi}^{(1)} = (\boldsymbol{p}_i - \boldsymbol{p}_f)\boldsymbol{F} \tag{8}$$

is the difference between the linear Stark shift of the neutral molecule (i) and that of its residual ion (f); $\boldsymbol{p}_\mu$ is the permanent dipole moment with respect to the center of the charge of the molecule or ion;

$$\Delta_{fi}^{(2)} = \tfrac{1}{2}\,(\alpha_i - \alpha_f)_{ij}F_iF_j \tag{9}$$

is the difference between quadratic Stark shifts of the energies of the neutral molecule and its ion; and $\hat{\alpha}_\mu = (\alpha_\mu)_{ij}$ is the dipole polarizability tensor. Summation over the repeated tensor indices ($i,j = x,y,z$) is applied in Eq. (9) and hereafter.

Accounting for (3) and (6), the tunneling rate changes to the following form:

$$W_{\mathrm{tot}}^{(\mathrm{dc})}(\theta,\phi,F) = \sum_{\{v_f\}}\sum_{m'} W_{m',fi}^{(\mathrm{dc})}(\theta,\phi,F). \tag{10}$$

Here,

$$\begin{aligned} W_{m',fi}^{(\mathrm{dc})}(\theta,\phi,F) &= \mathcal{I}_{fi}^{(v)2}\mathcal{I}_{fi}^{(e)2}\kappa_{fi}^2\exp[-2(p_{iz} - p_{fz})\kappa_{fi}] \\ &\quad\times \frac{|B_{m'}(\theta,\phi)|^2}{2^{|m'|}|m'|!}\left(\frac{2\kappa_{fi}^3}{F}\right)^{2\nu_{fi}-|m'|-1} \\ &\quad\times \exp\left(-\frac{2\kappa_{fi}^3}{3F}\right); \end{aligned} \tag{11}$$

$p_{\mu z}$ is the projection of $\boldsymbol{p}_\mu$ onto the direction of the electric-field vector $\boldsymbol{F}$; and

$$\kappa_{fi} = \nu_{fi}^{-1} = \left[2\left(I_{\mathrm{p}} + \Delta_{fi}^{(v)} + \Delta_{fi}^{(1)} + \Delta_{fi}^{(2)}\right)\right]^{1/2}. \tag{12}$$

The (θ,ϕ) angles define the spatial orientation of the molecule with respect to the electric-field vector $\boldsymbol{F}$, as follows. The rotation of the "molecular" reference frame by the angle θ about the "laboratory" y axis transfers the molecular quantization z' axis into the laboratory z axis directed along the $\boldsymbol{F}$ vector. After a subsequent rotation along the $z = z'$ axis by the angle ϕ, the molecular frame coincides with the laboratory one.

Equation (11) contains the angular factor

$$B_m(\theta,\phi) = \sum_{lm'} C_{lm'}D_{m'm}^{l}(0,\theta,\phi)Q_{lm'}, \tag{13}$$

where

$$Q_{lm} = (-1)^{(|m|-m)/2}\left[\left(l+\frac{1}{2}\right)\frac{(l+|m|)!}{(l-|m|)!}\right]^{1/2}.$$

The first argument of the Wigner D function in (13) is zero because the tunneling rate remains unchanged upon any rotation of the molecule about the direction of the electric-field vector.

The $\mathcal{I}_{fi}^{(v)2}$ quantities in Eq. (11) are the FCFs. Their values are determined not only by the vibrational quantum numbers, but also by other molecular vibrational parameters such as molecular geometry, normal vibration frequencies, potential energy surfaces, etc.

Formula (11) is derived in quasiclassical approximation which implies the following condition:

$$\kappa^3 \gg F. \tag{14}$$

Therefore, due to the $\exp[-2\kappa^3/(3F)]$ factor in Eq. (11), the tunnel-ionization rate is very sensitive to small changes of κ given by Eq. (12).

Due to the preexponential factor, $(2\kappa^3/F)^{-|m'|}$, the tunneling-ionization rate also depends strongly on the projection, m', onto the electric force. Namely, the ionization from the states with $|m'| \neq 0$ will be suppressed as compared to that from the state with $m' = 0$. Therefore, in Eq. (10), it is sufficient to hold the terms with $m' = 0$ only, as was done in Ref. [19],

$$W^{(\mathrm{dc})}(\theta,\phi;F) \approx \sum_{\{v_f\}} W^{(\mathrm{dc})}_{m'=0,fi}(\theta,\phi;F). \tag{15}$$

In this case, the expression (13) for B_0 is simplified:

$$B_0(\theta,\phi) = \sqrt{2\pi}\sum_{lm}(-1)^l C_{l,-m} Y_{lm}(\theta,\phi). \tag{16}$$

Let us now consider a linearly polarized monochromatic laser field,

$$\boldsymbol{F}(t) = \boldsymbol{F}_0 \sin\Omega t, \tag{17}$$

with the polarization vector $\boldsymbol{u} = \boldsymbol{F}_0/F_0$. Under the condition

$$\Omega\kappa_{fi}/F_0 < 1, \tag{18}$$

the ionization goes in the tunnel regime. The condition (18), as a rule, is satisfied for a laser radiation in the NIR range with an intensity of $\sim 10^{14}$ W/cm^2, which can be generated by the available powerful laser facilities. It is well known (see Refs. [52,53]) that in this case, the Born-Fock adiabatic approximation can be used. This approximation consists of the following substitution in Eq. (10):

$$\boldsymbol{F} \to \boldsymbol{F}_0 \sin\Omega t. \tag{19}$$

The current ionization rate, $W(\sin\Omega t)$, obtained from Eq. (10) under the substitution (19), should be averaged over the optical cycle of laser radiation,

$$W^{(\mathrm{ac})}(\theta,\phi;F_0) = \frac{1}{2\pi}\left[\int_0^{\pi} W(\sin\xi)\,d\xi + \int_{\pi}^{2\pi} W(\sin\xi)\,d\xi\right]. \tag{20}$$

In Eq. (20), the orientation of the molecule is defined with respect to the polarization vector $\boldsymbol{u}$. The integral over the optical cycle of laser radiation is represented as a sum of two integrals over half cycles corresponding to two antiparallel directions of the electric-field vector. The projections of the permanent dipole moment, $p_{\mu z}$, have opposite signs for two subsequent half cycles.

The condition (14) permits using the saddle-point method in calculating the integral in Eq. (20):

$$W^{(\mathrm{ac})}(\theta,\phi;F_0) \approx \frac{1}{2}\sum_{\{v_f\}}\Big[W^{(\mathrm{dc})}_{0,fi}(\theta,\phi;F_0) + W^{(\mathrm{dc})}_{0,fi}(\pi-\theta,\pi+\phi;F_0)\Big]\sqrt{\frac{3F_0}{\pi\kappa_{fi}^3}}. \tag{21}$$

Each term in the sum in Eq. (21) is given by the expression (11). For the molecules with an inversion center, Eq. (21) turns into the form used in MO-ADK theory [17] under neglect of the internal degrees of freedom.

Equation (21) is the key formula in this section. It can be used not only for monochromatic radiation, but also for a laser pulse with $\gtrsim 5$ cycles. For such a pulse, the following substitution should be made in Eq. (21):

$$F_0 \to F_0 f(t),$$

where $f(t)$ is the electric-field envelope in the laser pulse. To obtain the total ion yield in the laser pulse (i.e., ionization signal), an integration should be performed over the focal volume of the laser beam. A method of such an integration proposed in Ref. [54] was adapted for molecules in Ref. [24].

IV. DEFORMATION OF AN A_2B MOLECULE IN A LASER FIELD

In this section, we consider deformation of a symmetric A_2B molecule under the influence of an ionizing laser field.

A. Normal vibrations

First, we find the normal coordinates and reduced masses of a symmetric nonlinear triatomic A_2B molecule in the absence of internal fields. Our analysis of vibrational motion is based on Refs. [55–57].

Let m_A and m_B be the nuclei masses, with l being the equilibrium A–B bond length and 2γ being the bending angle. We choose the Cartesian reference frame with the origin at the B atom and z axis directed along the molecular symmetry axis so that the molecule is placed in the yz plane. It is convenient to define the deformation of the molecule by its nuclei displacement vectors, $\boldsymbol{u}_{1,3} = \{y_{1,3}, z_{1,3}\}$ for A nuclei and $\boldsymbol{u}_2 = \{y_2, z_2\}$ for B nucleus (see Fig. 1). These displacements are assumed to be small compared with the bond length. Note that the molecule remains planar for any deformation.

After the translational and rotational motions of the molecule as a whole are excluded, the Lagrangian of the molecule's vibrational motion takes the form

$$\mathcal{L}^{(0)}_{A_2B} = \mathcal{L}_s + \mathcal{L}_b + \mathcal{L}_a, \tag{22}$$

where

$$\mathcal{L}_j = \tfrac{1}{2}M_j\dot{Q}_j^2 - \tfrac{1}{2}M_j\omega_j^2 Q_j^2, \quad j = s,b,a.$$

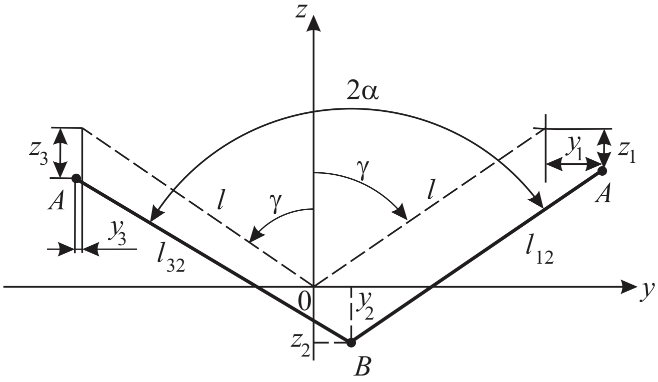

FIG. 1. Deformation of an A_2B molecule in Cartesian coordinates.

The Lagrangian (22) corresponds to three independent linear harmonic oscillators, or normal modes, with the frequencies $\omega_{s,b,a}$ and with the corresponding reduced masses $M_{s,b,a}$. The first two terms of Eq. (22) describe the symmetric stretch (s) and bending (b) vibrations, which have A_1 symmetry (see Fig. 2). The last term of Eq. (22) corresponds to antisymmetric (a) stretch vibration, which has B_2 symmetry (see Fig. 3).

The Cartesian components of the $\boldsymbol{u}_{1,2,3}$ vectors are expressed in terms of the normal coordinates $Q_{s,b,a}$ as follows:

$$\begin{aligned} y_1 &= \frac{1}{2}(Q_a + Q_s + Q_b), \\ z_1 &= \frac{1}{2}(f_s Q_s + f_b Q_b + Q_a \cot\gamma), \\ y_2 &= -\frac{m_A}{m_B} Q_a, \quad z_2 = -\frac{m_A}{m_B}(Q_s + Q_b), \\ y_3 &= \frac{1}{2}(Q_a - Q_s - Q_b), \\ z_3 &= \frac{1}{2}(f_s Q_s + f_b Q_b - Q_a \cot\gamma). \end{aligned} \tag{23}$$

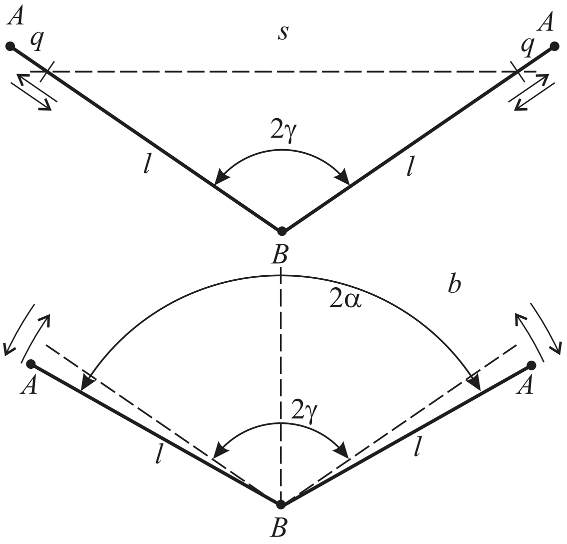

FIG. 2. Symmetric—stretch s and bending b—normal vibrations of an A_2B molecule.

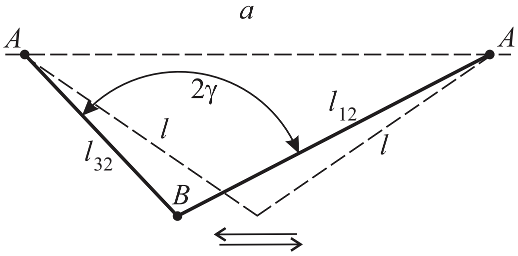

FIG. 3. Antisymmetric, a, stretch normal vibration of an A_2B molecule.

The analytic expression of the $f_{s,b}$ factor is rather complicated and is given in Appendix A.

The reduced masses $M_{s,b,a}$ are given by

$$\begin{aligned} M_s &= \frac{1}{2} m_A \left(1 + f_s^2 \frac{M}{m_B}\right), \\ M_b &= \frac{1}{2} m_A \left(1 + f_b^2 \frac{M}{m_B}\right), \\ M_a &= \frac{1}{2} m_A \left(\frac{2m_A}{m_B} + \frac{1}{\sin^2\gamma}\right), \end{aligned} \tag{24}$$

where

$$M = 2m_A + m_B \tag{25}$$

is the mass of the molecule.

Note that the choice of the normal coordinates is not unique: indeed, the Lagrangian (27) is invariant to a simultaneous scaling of a reduced mass M_j and the corresponding normal coordinate Q_j:

$$Q_j \to Q_j/\beta, \quad M_j \to \beta^2 M_j, \tag{26}$$

where β is an arbitrary positive constant.

B. Laser-induced modification of vibrational parameters: General formalism

In this section, we consider modification of geometric parameters of polyatomic molecules in an ac electric field. This modification is due to the molecular polarizability which determines the potential energy of the molecule in the field. Therefore, the equilibrium configuration of the molecule in the field should differ from the equilibrium configuration of a free molecule. Our consideration uses the results of Ref. [58].

We denote the molecular normal coordinates as $\mathbf{Q} = \{Q_1, Q_2, \ldots, Q_n\}$, where n is the number of the vibrational degrees of freedom. In these coordinates, the Lagrangian of classical vibrational motion is the sum of the Lagrangians of independent harmonic oscillators [56,59]:

$$\mathcal{L}_0 = \frac{1}{2}\sum_{k=1}^{n} M_k \dot{Q}_k^2 - \frac{1}{2}\sum_{k=1}^{n} M_k \omega_{0k}^2 (Q_k - Q_{ek})^2. \tag{27}$$

Here, ω_{0k} is the frequency of the kth normal vibrational mode, Q_{ek} is the equilibrium value of the normal coordinate Q_k, and M_k is the reduced mass corresponding to the kth mode. We assume the absence of degenerate oscillations (it is the case for nonlinear A_2B).

The further consideration is based on the method proposed by Kern and Matcha [41] and developed by Pandey and Santry [42] to account for nonadiabatic effects in the optical properties of molecules.

The change of the vibrational parameters in an external linearly polarized field (17) is due to the transformation of the potential energy surface (PES) because of the ac Stark shift. To the second-order terms $\sim F_0^2$, this shift is determined by the molecular dynamic dipole polarizability, $\alpha_{ij}(\Omega)$:

$$\Delta E_{\text{Stark}} = -\tfrac{1}{4}\alpha_{ij}F_{0i}F_{0j}. \tag{28}$$

The polarizability α_{ij} depends on the normal coordinates $\{Q_k\}$ and the laser-field frequency Ω. Therefore, with the use of (28), the PES equation can be expanded in the Taylor series (up to quadratic terms),

$$\begin{aligned}\mathcal{U}(\mathbf{Q}) \approx \frac{1}{2}\sum_k M_k\omega_{0k}^2(Q_k - Q_{ek})^2 \\ -\frac{1}{4}F_{0i}F_{0j}\Bigg[\alpha_{ij}^{(0)} + \sum_k \alpha_{ij}^{(1k)}(Q_k - Q_{ek}) \\ + \frac{1}{2}\sum_{kk'}\alpha_{ij}^{(2kk')}(Q_k - Q_{ek})(Q_{k'} - Q_{ek'})\Bigg].\end{aligned} \tag{29}$$

Here, $\alpha_{ij}^{(0)}$ is the polarizability at the equilibrium values of the normal coordinates $\{Q_{ek}\}$,

$$\alpha_{ij}^{(1k)} = \frac{\partial\alpha_{ij}}{\partial Q_k}\bigg|_{Q_l=Q_{el}}, \quad \alpha_{ij}^{(2kk')} = \frac{\partial^2\alpha_{ij}}{\partial Q_k\partial Q_{k'}}\bigg|_{Q_l=Q_{el}},$$
$$l = 1,2,\ldots,n.$$

Unlike Eq. (27), the laser-modified Lagrangian include linear terms $\sim(Q_i - Q_{ei})$ and the Hessian of the potential energy (29),

$$\frac{\partial^2\mathcal{U}}{\partial Q_k\partial Q_{k'}}\bigg|_{Q_l=Q_{el}} = M_k\omega_{0k}^2\delta_{kk'} + \frac{1}{4}\alpha_{ij}^{(2kk')}F_{0i}F_{0j},$$

is not a diagonal quadratic form. However, its off-diagonal elements have the smallness of $\sim F_0^2$, and therefore after a proper shift $\sim F_0^2$ of the equilibrium coordinates,

$$Q_{Ek} \approx Q_{ek} + \frac{\alpha_{ij}^{(1k)}F_{0i}F_{0j}}{4M_k\omega_{0k}^2}, \tag{30}$$

the Lagrangian with (29) can be diagonalized and

$$\omega_k^2 \approx \omega_{0k}^2 - \frac{\alpha_{ij}^{(2kk)}}{4M_k}F_{0i}F_{0j}. \tag{31}$$

Equations (31) and (30) solve the problem imposed in this section. The field-modified frequencies differ from those of a free molecule by small corrections. The molecular normal coordinates in the laser field differ from the free-molecular ones by small shifts of the equilibrium positions. The expressions (31) and (30) are the counterparts of those obtained in [40] for diatomics. They show that the field-induced changes in normal modes of polyatomics with nondegenerated normal modes are independent provided that only the lowest (quadratic) order of the Stark effect is considered.

C. Laser-induced modification of vibrational parameters: A_2B molecule

For the case of a triatomic nonlinear symmetric molecule, one should assume $k = a,\ s,\ b$ in the expressions (30) and (31). For simplicity, the origins of the normal coordinates are convenient to be chosen in the equilibrium positions of the nuclei: $Q_{\text{es}} = Q_{\text{eb}} = Q_{\text{ea}} = 0$.

For the antisymmetric stretch (a) vibrations, we have

$$\frac{\partial\hat{\alpha}}{\partial Q_a}\bigg|_0 = 0$$

due to the symmetry of the A_2B molecule with respect to the bisectrix of the bending angle. Therefore, to the first approximation in the radiation intensity, laser-induced deformations of a molecule are possible only due to a shift of the equilibrium positions of the symmetric (s, b) vibrations. In particular, the modification of the A–B bond length is

$$\begin{aligned}\Delta l \approx \frac{1}{2}\bigg[\bigg(\sin\gamma + f_s\frac{M}{m_B}\cos\gamma\bigg)Q_{Es} \\ + \bigg(\sin\gamma + f_b\frac{M}{m_B}\cos\gamma\bigg)Q_{Eb}\bigg],\end{aligned} \tag{32}$$

and the modification of the bending angle is

$$\begin{aligned}\Delta\cos 2\gamma \approx -\frac{\sin 2\gamma}{l}\bigg[\bigg(\cos\gamma - f_s\frac{M}{m_B}\sin\gamma\bigg)Q_{Es} \\ + \bigg(\cos\gamma - f_b\frac{M}{m_B}\sin\gamma\bigg)Q_{Eb}\bigg].\end{aligned} \tag{33}$$

Formulas (32) and (33) are derived from Eqs. (23) assuming that the modifications are small.

The laser-induced shifts Q_{Ek} allow one to obtain the laser-modified values of the Franck-Condon factors. For details, see Appendix B.

V. NUMERICAL RESULTS

The rate of tunnel ionization of a molecule by monochromatic laser radiation is calculated with the help of Eq. (21) taking into account Eq. (12). The vibrational overlap integrals $\mathcal{I}^{(v)}$ and FCFs are calculated using Eq. (B8). The electronic overlap integrals are calculated according to the formulas of the Appendix to Ref. [15].

As examples, we considered symmetric nonlinear molecules H_2O, SO_2 and the H_2O^+ ion. Table I lists the vibrational parameters of all the considered molecules and ions. The normal vibration frequencies are given, e.g., in Ref. [60]. The other vibrational parameters were calculated using the GAUSSIAN package. In their study of the CO_2 molecule, Kono *et al.* [61] proposed to use configuration-interaction methods with Pople's 6-311G(d) basis set. In the present paper, we use the quadratic configuration-interaction single-double excitation (QCISD) method with an equivalent cc-pVQZ basis set, which can be used for the polarizability calculation unlike the Pople's sets. The electromagnetic parameters (dipole moments and polarizabilities) of the considered molecules and ions are given in Table II.

The modifications of the molecular vibrational parameters (normal frequencies and equilibrium positions) in a

TABLE I. The frequencies of the normal coordinates, bond lengths l, and bending angles 2γ, in symmetric triatomic molecules and their ions.

Molecule	ω_a (cm^{-1})	ω_s (cm^{-1})	ω_b (cm^{-1})	l (Å)	2γ
H_2O[a]	3942.5	3832.2	1648.5	0.958	104.4776°
H_2O[b]	3984.4	3879.8	1670.4	0.956	104.3637°
H_2O^{+}[b]	3472.7	3418.7	1483.7	0.997	109.4566°
H_2O^{2+}[b]	1862.2	1462.3	815.6	1.177	125.2367°
SO_2[a]	1380.91	1167.6	526.27	1.432	119.5°
SO_2[b]	1409.76	1209.3	536.59	1.432	118.8225°
SO_2[a]	1227.73	1074.3	409.15	none	none
SO_2[b]	1253.38	1112.7	417.17	1.423	131.9789°

[a] From Ref. [60].

[b] From GAUSSIAN with QCISD/cc-pVQZ.

TABLE III. Relative changes of the normal vibration frequencies $\Delta(\omega_i) = \Delta\omega_i/\omega_i$, bond lengths $\Delta(l) = \Delta l/l$, and bending angles $\Delta(\gamma) = \Delta\gamma/\gamma$ (in %) for symmetric nonlinear triatomic molecules and their ions in a monochromatic linearly polarized laser field with an intensity of 10^{14} $\mathrm{W/cm^2}$.

Molecule	$\Delta(\omega_a)$	$\Delta(\omega_s)$	$\Delta(\omega_b)$	$\Delta(l)$	$\Delta(\gamma)$
			$\boldsymbol{u} = \boldsymbol{e}_x$		
H_2O	−0.0044	+0.018	−0.028	+0.090	+0.012
H_2O^{+}	−2.553	−.3742	−.8737	+0.5077	−0.0372
H_2O^{2+}[a]	+1.081	−0.2773	−1.157	+1.734	−0.1717
SO_2	−0.1020	−0.1733	−0.4133	+0.0560	+0.1660
SO_2^{+}	−0.2045	+0.0077	−0.6855	+0.1191	+0.0070
			$\boldsymbol{u} = \boldsymbol{e}_y$		
H_2O	−0.37	−0.73	−1.33	+0.61	+0.53
H_2O^{+}	−2.332	−5.195	−8.947	+4.820	+4.640
H_2O^{2+}[a]	+5.223	−18.09	−11.05	+27.68	+8.013
SO_2	−2.689	−0.6280	−0.4133	+0.7295	+0.8999
SO_2^{+}	−5.112	−1.438	−10.88	−0.2573	+0.6316
			$\boldsymbol{u} = \boldsymbol{e}_z$		
H_2O	−0.26	−0.26	−0.87	+0.37	+0.012
H_2O^{+}	−1.266	−1.870	−7.529	+2.439	−5.802
H_2O^{2+}[a]	+1.153	−5.173	−10.59	+10.03	−12.74
SO_2	−0.66646	−0.3259	−1.031	+0.1751	−0.6804
SO_2^{+}	−0.2364	+0.4528	−0.8767	+0.1609	−0.9900

[a] For an intensity of 10^{15} $\mathrm{W/cm^2}$.

monochromatic linearly polarized laser field are calculated using Eqs. (30) and (31). The modifications of the bond lengths and bending angles are calculated using Eqs. (32) and (33), respectively. In the calculations, we used the static values of the polarizabilities which differ little from their dynamic values in the NIR range of the radiation. The differentiation of the polarizability, $\hat{\alpha}$, with respect to the normal coordinates is performed using five sample points with a step of 0.005 Å. The results of these calculations by formulas (31)–(33) for the laser radiation intensity of 10^{14} $\mathrm{W/cm^2}$ and several directions of its polarization vector $\boldsymbol{u}$ are presented in Table III for H_2O, H_2O^+, and SO_2 molecules. The GAUSSIAN package with QCISD/cc-pVQZ was used in these calculations. As seen from Table III, the most significant modification of the vibrational parameters takes place when the polarization vector lies in the molecular plane. It is also seen that the most significant laser-induced bent of the molecules (i.e., decrease of the bending angle) corresponds to the case when the polarization vector is parallel to the molecular symmetry axis. The other directions of the polarization vector result, as a rule, in "straightening" of the molecules.

The structure factors C_{lm} [see Eq. (5)] are needed to study the tunnel ionization of molecules. Their values are known [18,21] but should be recalculated to the dimensionless form (5) for the orientation according to Fig. 1. The dimensionless structure factors C_{lm} obtained in the present paper are given in Tables IV and V.

In spite of the geometric similarity of the H_2O and SO_2 molecules, they have principally different electronic structures. First, all the electronic orbitals in the H_2O molecule have odd projections Λ of the orbital angular momentum onto the symmetry axis. On the contrary, all of the electronic orbitals of the SO_2 molecule are characterized by even Λ (see Tables IV and V). It means that all of the orbitals of the water molecule lack a contribution from the electronic σ states.

Second, due to the high electronegativity of oxygen, this atom carries an excess negative Mulliken charge in both molecules. Therefore, their permanent dipole moments $\boldsymbol{p}_i$ have opposite directions. In the water molecule, $\boldsymbol{p}_i$ is directed from the O atom to the center of the H–H line. On the contrary, in the sulfur dioxide molecule, $\boldsymbol{p}_i$ is directed from the center of the O–O line to the S atom (see Table II).

The tunnel-ionization rate is calculated with the help of Eq. (21). It is interesting to show an example of electronic

TABLE II. The components (in the major axes) of polarizability tensor $\hat{\alpha}$ (in Bohr^3) and the permanent dipole moment vector $\boldsymbol{p}$ (in D) for symmetric triatomic molecules and its ions, calculated by GAUSSIAN with QCISD/cc-pVQZ. The molecular orientation is shown in Fig. 1 (with z directed along the bisectrix of the bending angle, and the x axis perpendicular to the molecule's plane). The origin of the reference frame is placed in the center of nuclear charge.

	H_2O	H_2O^{+}	H_2O^{2+}	SO_2	SO_2^{+}
p_z[a]	1.855	none	none	−1.630	none
p_z	1.905287	2.114637	2.927798	−1.745838	−1.294614
α_{xx}	6.605699	3.965230	2.982851	16.896724	14.225520
α_{yy}	8.767866	6.184936	5.713475	31.730373	31.972589
α_{zz}	7.916490	4.940379	3.914259	20.357304	17.026385

[a] From Ref. [60].

TABLE IV. The structure factors C_{lm} for the H_2O molecule extracted from Ref. [21] and recalculated to the dimensionless form (5) for the orientation according to Fig. 1.

l	$m = 1$	$m = 3$	$m = 5$
1	1.984		
2	1.476×10^{-1}		
3	-1.211×10^{-2}	3.602×10^{-2}	
4	-3.096×10^{-4}	-7.053×10^{-3}	
5	7.430×10^{-5}	5.212×10^{-4}	-2.602×10^{-4}

TABLE V. Same as in Table IV, but for an SO_2 molecule. The data are extracted from Ref. [18].

l	$m = 0$	$m = 2$	$m = 4$
0	3.19		
1	0.80		
2	1.38	−0.06	
3	−0.91	−0.76	
4	−0.35	−0.31	0.05
5	0.05	0.08	0.13
6	0.08	0.06	0.05

overlap integrals $\mathcal{I}_{fi}^{(e)}$ in the Dyson orbitals (3),

$$\mathcal{I}_{fi}^{(e)}[\mathrm{H_2O}] = 0.997, \quad \mathcal{I}_{fi}^{(e)}[\mathrm{SO_2}] = 0.653.$$

Such a significant difference is due to the large difference in bending angles between the SO_2 molecule and its ion SO_2^+ (see Table I).

The algorithm of the calculation of the vibrational overlap integrals, $\mathcal{I}_{fi}^{(v)}$, for a symmetric nonlinear A_2B molecule is given in Appendix B. This algorithm uses the laser-modified vibrational parameters as input data.

For simplicity, we restrict ourselves to the tunnel transitions between the ground vibrational states ($v_{\mathrm{ai}} = v_{\mathrm{si}} = v_{\mathrm{bi}} = v_{\mathrm{af}} = v_{\mathrm{sf}} = v_{\mathrm{bf}} = 0$). The further considerations are convenient to be performed separately for each molecule.

A. Ionization of H_2O molecule

Here we consider tunnel ionization of a neutral H_2O molecule with a prescribed orientation with respect to the linear polarization vector of a monochromatic laser radiation (the definition of this orientation is described in Sec. III). Our calculations show that the most significant influence of the laser-induced deformation on tunnel ionization via FCFs will be attained when the polarization vector lies in the molecule plane, i.e., when $\phi = 90^\circ$. We calculated the ratio between the ionization rates of laser-field deformed and nondeformed molecules as a function of the intensity of the monochromatic laser radiation for several values of the θ angle (recall that θ is the angle between the molecular axis and the polarization vector).

The results of the calculation are presented in Fig. 4. In spite of the increasing influence of the ω_b modification with the decrease of θ, the contribution of this modification into the tunnel-ionization rate is less than 3% for the H_2O molecule.

B. Ionization of H_2O^+ ion

The calculation of the structural factors, C_{lm}, is a nontrivial task. To perform it, as a rule, one should first simulate the molecular electronic structure with "frozen" nuclei, i.e., using the Gaussian orbital method. Then one can use density functional theory with B splines [18] or direct calculation with the polarization-consistent basis sets adopted for each molecule individually [21]. The calculation of structural factors is beyond the scope of the present work, and thus we use the known results for C_{lm} when available.

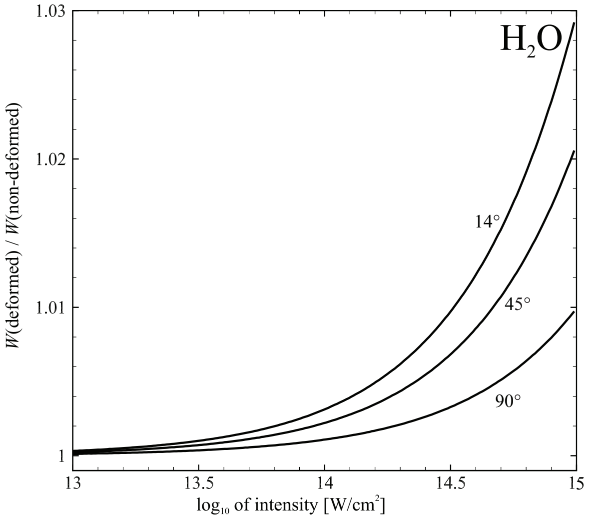

FIG. 4. The ratio between the ionization rates of laser-field deformed and nondeformed H_2O molecules. The polarization vector of the monochromatic laser radiation is parallel to the molecule plane. The curves are labeled by the angle θ between the molecular axis and the polarization vector.

Since the structure factors C_{lm} are unknown for the H_2O^+ ion, we calculated the ratio between FCFs of a laser-field deformed and nondeformed H_2O^+ ion. The results are shown in Fig. 5.

The difference between the vibrational parameters of the H_2O^+ and H_2O^{2+} ions is greater than that between the parameters of the neutral H_2O molecule and H_2O^+ ion (see Table I). Higher intensities are required for tunnel ionization of H_2O^+ as compared to the neutral H_2O molecule. Therefore, the laser-induced deformation of the H_2O^+ ion is more significant

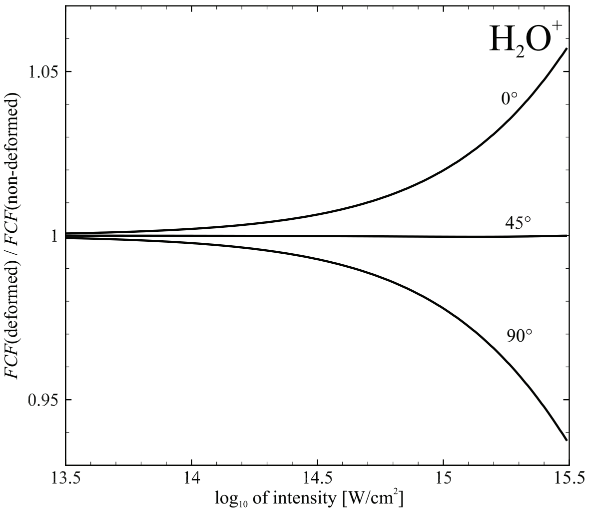

FIG. 5. The ratio between the Franck-Condon factors of a laser-field deformed and nondeformed H_2O^+ ion. The polarization vector of the monochromatic laser radiation is parallel to the molecular ion plane. The curves are labeled by the angle θ between the molecular axis and the polarization vector.

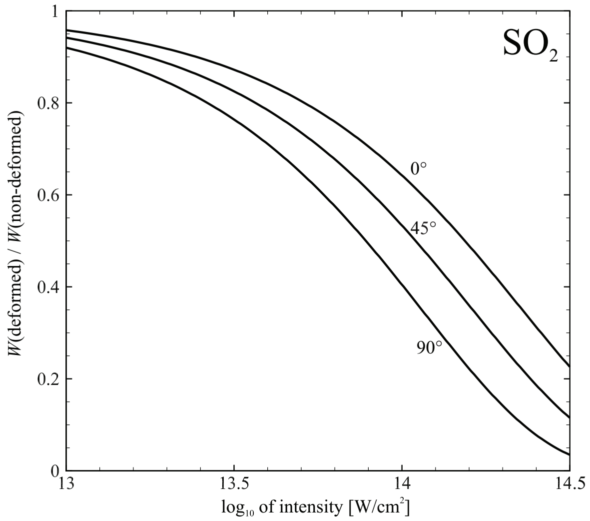

FIG. 6. Same as in Fig. 4, but for an SO$_2$ molecule.

compared to that of the neutral molecule (see Table III), and the relative change in FCFs attains ±5%.

C. Ionization of SO$_2$ molecule

The ionization of the SO$_2$ molecule was considered at the same conditions as for H$_2$O. The results for the ratios between the ionization rates of laser-field deformed and nondeformed SO$_2$ molecules are given in Fig. 6. Unlike the case of the water molecule, accounting for the laser-induced deformation of sulfur dioxide can change the tunnel-ionization rate by up to ∼20 times. We suppose that such a sharp distinction is due to significant differences in the electronic structure of these molecules (see the discussion of Tables II, IV, and V), as well as to nonmonotonic FCF dependence on the molecular geometry and vibrational frequencies [62].

The influence of the permanent dipole moment on the ionization via the linear Stark effect will be maximal when the polarization vector is parallel to the permanent dipole moment vector [see Eqs. (11) and (21)]. For the sulfur dioxide, the permanent dipole moment results in an increase of the tunnel-ionization rate by 16%. For the water molecule of the same orientation, the tunnel ionization is suppressed due to nonzero projections of the orbital angular momentum onto the symmetry axis (see Table V). The most effective tunnel ionization of the water molecule takes place when the polarization vector is perpendicular to the symmetry axis so that the influence of the permanent dipole moment is absent.

At intensities far from saturation, i.e., $I \lesssim 10^{16}$ W/cm^2, the ionization probability for the SO$_2$ molecule, taking into account its laser-induced deformation, can be approximated, within a $\sim eq1\%$ accuracy, by the following dependence:

$$W(I) = W_0(I/I_0)^k f_{\mathrm{FC}}(I) \exp\left(-\sqrt{I_0/I}\right),$$

$$f_{\mathrm{FC}}(I) = \frac{1}{[1+(I/I_1)^{\alpha}]^2}, \quad I_0 = 1.16\times10^{16}\ \mathrm{W/cm^2}. \tag{34}$$

The parameters k,α, and I_1 are given in Table VI for several angles. It is interesting to note that $I_1 \ll I_0$. It means that the deformation becomes significant in sufficient low-intensity field, i.e., when the tunnel ionization of the molecule has a low probability.

TABLE VI. The values of W_0, k, α, and I_1 parameters in formula (34) for some values of the orientation angle θ.

θ	W_0	k	α	I_1 10^{14} (W/cm^2)
0°	13.19	−0.35	1.07	3.75
45°	5.08	−0.33	1.10	2.54
90°	1.22×10^{-2}	−0.29	1.14	1.70

Due to high sensitivity of the tunnel-ionization rate of SO$_2$ to the laser-induced deformation, it is interesting to make some estimations for the quantities measured in a real experiment. We calculate the signal from a detector of SO$_2^+$ ions in a focal volume of a laser-beam pulse. There exists several methods for controlling the molecular orientation in a gas phase (see, e.g., [63]). We choose a close-to-real model of a Gaussian beam with a Gaussian time envelope having FWHM of about 100 fs. For such a short pulse duration, the orientation of molecules attained during the laser pulse remains unchanged after the pulse has passed [17]. The results of the ion signal as a function of the peak intensity in the focal volume are presented in Fig. 7. Similarly to the ionization rate, the influence of the molecule deformation on the ion yield increases monotonically with the increase of θ. While accounting for the molecule deformation by a laser radiation with the intensity of 3.16×10^{14} W/cm^2 lowers the ion yield by 20% at $\theta = 0°$, such an account will rise the ion yield by five times at $\theta = 90°$.

Note that after having performed an averaging on the spatial orientations of the SO$_2$ molecule, the contribution of the

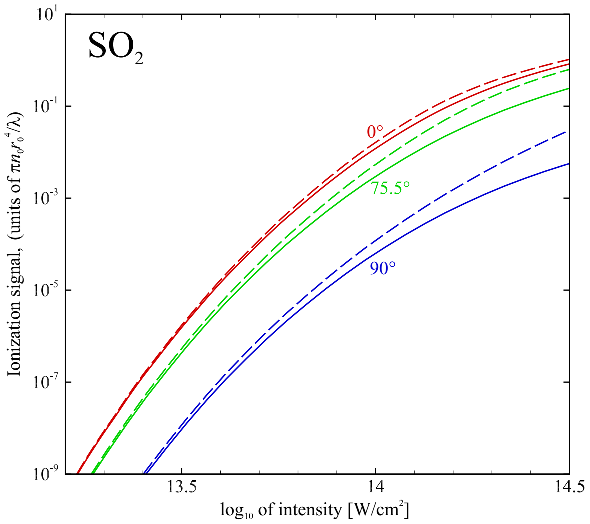

FIG. 7. Ionization signal from SO$_2$ molecules oriented in a focal volume of a laser beam. Here, n_0 is the concentration of neutral-oriented molecules, r_0 is the radius of the beam "waist" in the focal volume, and λ is the central wavelength of radiation on the laser pulse. FWHM is chosen to be of 100 fs. Solid lines: the results taking into account the laser-induced deformation of the molecules; dashed lines: the results for nondeformed molecules. The curves are labeled by the angle θ between the molecular axis and the polarization vector.

permanent dipole moment into the ionization signal will be reduced to 5%, while for the case of the H_2O molecule, this contribution of the permanent dipole moment will not exceed 1%.

Given such an essential influence of the laser-induced deformation of the SO_2 molecule on its tunnel ionization, it is advisable to estimate the contribution of fourth-order Stark-shift terms $\sim F^4$ in the molecule deformation. According to Maroulis [64], the second hyperpolarizability averaged over the spatial orientations of the SO_2 molecule is $\bar{\gamma} = 2038$ a.u. Then the corresponding Stark-shift term is $\overline{\Delta E^{(4)}} = (1/64)\bar{\gamma}F^4$. The $\overline{\Delta E^{(4)}}/\overline{\Delta E^{(2)}}$ ratio is about 0.02 at an intensity of 10^{14} W/cm^2 and about 0.05 at an intensity of 3.16×10^{14} W/cm^2. Thus, it is the quadratic Stark term, $\overline{\Delta E^{(2)}}$, which play the leading role in the laser-induced deformation of the SO_2 molecule.

VI. CONCLUSION

Unlike atoms, the ionization of molecules requires substantial modifications of Keldysh theory at least in three ways, to account for (i) a dependence of the ionization rate on the molecular orientation, (ii) vibrational degrees of freedom, and (iii) an essential role of the linear Stark effect which arise in some molecules due to the permanent dipole moment. This research aims to theoretically study the light-dressing effect in molecules, in particular, of the laser-induced deformation of polyatomic molecules, and to account for the influence of this effect on the tunnel ionization of molecules. A theoretical description of monochromatic laser-induced modification of geometry and vibrational parameters of a polyatomic molecule is given. As an example, we consider the deformation of a symmetric nonlinear molecule of the A_2B type with the explicit formulas accounting for the influence of molecular deformation on the Franck-Condon factors.

The numerical calculations are done for H_2O, H_2O^+, and SO_2 molecules. For the H_2O molecule, the contribution of laser-induced deformation into the tunnel-ionization rate is less than 3%. The deformation of the H_2O^+ ion is slightly more significant, and the relative change in Franck-Condon factors attains ±5%. But, unlike the case of a water molecule, taking into account laser-induced deformation of SO_2 can change the tunnel-ionization rate by up to ~20 times. Such a sharp distinction is due to significant differences in the electronic structure of these molecules as well as to the nonmonotonic dependence of Franck-Condon factors on the molecular geometry and vibrational frequencies.

We also calculate the signal from a detector of SO_2^+ ions in a focal volume of a Gaussian laser-beam pulse with a duration of about 100 fs. The influence of laser-induced deformation on the ion signal depends critically upon the angle θ between the molecular axis and the polarization vector of the laser radiation.

ACKNOWLEDGMENTS

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APPENDIX A: EXPLICIT FORMULAS FOR $f_{s,b}$ FACTORS

The factors $f_{s,b}$ appearing in Eqs. (23) and (24) have the following form:

$$f_s = -\frac{m_B}{M}\frac{\omega_s^2 - (\lambda_1 \sin^2\gamma + \lambda_2 \cos^2\gamma)}{(\lambda_2 - \lambda_1)\sin\gamma\cos\gamma},$$
$$f_b = -m_B/(M f_s). \tag{A1}$$

Here, M is given by Eq. (25),

$$\lambda_1 \equiv \frac{k_1}{m_A} = \frac{\omega_s^2 + \omega_b^2 + \lambda_0^2}{2\left(1 + \frac{2m_A}{m_B}\cos^2\gamma\right)},$$
$$\lambda_2 \equiv \frac{2k_2}{m_A} = \frac{\omega_s^2 + \omega_b^2 - \lambda_0^2}{2\left(1 + \frac{2m_A}{m_B}\sin^2\gamma\right)},$$
$$\lambda_0^4 = (\omega_s^2 + \omega_b^2)^2 - \frac{4m_B}{M}\omega_s^2\omega_b^2\left(1 + \frac{2m_A}{m_B}\cos^2\gamma\right)$$
$$\times\left(1 + \frac{2m_A}{m_B}\sin^2\gamma\right). \tag{A2}$$

APPENDIX B: FRANCK-CONDON FACTORS

Accounting for the anharmonicity of vibrations in polyatomic molecules is quite a hard task because each normal vibration displays not only its own anharmonicity, but also mutual anharmonicity between different normal modes can occur. For this reason, FCFs are calculated in the present paper in harmonic approximation using the generating function method proposed by Sharp and Rosenstock [62].

First we consider a general case of a molecule with n nondegenerate vibrational degrees of freedom. It is convenient to choose so called mass-weighted normal coordinates, i.e., to choose the following scaling factor in Eq. (26):

$$\beta_k = 1/\sqrt{M_k}, \tag{B1}$$

which results in unity masses for all the normal oscillators in the molecule.

Let the vector $\mathbf{Q}' \equiv \{Q_1', Q_2', \dots, Q_n'\}$ denote the set of all of the mass-weighted normal coordinates of the molecule, with $\mathbf{v} \equiv \{v_1, v_2, \dots, v_n\}$ being the corresponding vibrational quantum numbers and $\hat{\Gamma} \equiv \mathrm{diag}(\omega_1, \omega_2, \dots, \omega_n)$ being the diagonal matrix of the normal frequencies.

The FCF $\mathcal{I}(v)_{fi}(\mathbf{v}_f, \mathbf{v}_i)$ is defined by the relation (4), in which the integration should be done over the normal coordinates. To this end, the normal coordinates $\mathbf{Q}_i'$ of the initial state (neutral molecule) should be expressed in terms of the normal coordinates $\mathbf{Q}_f'$ of the final state (residual molecular ion). This linkage is linear and it has a form of

$$\mathbf{Q}_i' = \hat{J}\mathbf{Q}_f' + \mathbf{K}. \tag{B2}$$

The $\hat{J}$ matrix and $\mathbf{K}$ vector entering Eq. (B2) are to be obtained in terms of the variations of internal coordinates $\mathbf{S}$ (bond lengths, bending, out-of-plane wagging, torsion angles, etc.) with respect to their equilibrium positions $\mathbf{S}_e$. For sufficiently small variations, they are linearly related to the normal coordinates,

$$\mathbf{S}_\mu = \hat{L}_\mu \mathbf{Q}'_\mu, \quad \mu = i, f, \tag{B3}$$

where the matrix $\hat{L}_\mu$ gives the transition from the normal coordinates to the internal ones. The $\hat{L}_\mu$ matrix is determined by the equilibrium configuration of the molecule. The displacements of atoms in the neutral molecule are linked to those in the residual ion by the following simple relation:

$$\mathbf{S}_i = \mathbf{S}_f + \Delta\mathbf{S}, \quad \Delta\mathbf{S} = \mathbf{S}_{ef} - \mathbf{S}_{ei}, \tag{B4}$$

where $\mathbf{S}$ is the displacement of the equilibrium positions of the internal coordinates. The substitution (B4) in (B3) results in the following formulas for $\hat{J}$ and $\mathbf{K}$:

$$\hat{J} = \hat{L}_i^{-1}\hat{L}_f, \quad \mathbf{K} = \hat{L}_i^{-1}\Delta\mathbf{S}. \tag{B5}$$

Under the influence of the laser radiation, the equilibrium positions of the normal oscillators are displaced according to Eq. (30). In this case, according to Eqs. (B3) and (B4), the quantity

$$\Delta\mathbf{S} = \mathbf{S}_{ef} - \mathbf{S}_{ei} + \hat{L}_f\mathbf{S}'_{Ef} - \hat{L}_i\mathbf{S}'_{Ei} \tag{B6}$$

depends on the laser field strength and the molecule orientation via the mass-weighted displacements of the equilibrium positions, $\mathbf{Q}'_{E\mu} \equiv \{Q'_{E\mu,1}, Q'_{E\mu,2}, \ldots, Q'_{E\mu,n}\}$, of the normal oscillators:

$$Q'_{E\mu,k} = \frac{\alpha^{(1k)}_{\mu,ij} F_{0i} F_{0j}}{4M_{k\mu}^{1/2}\omega_{0k\mu}^2}, \quad \mu = i, f. \tag{B7}$$

A particular case, which is important for the present work, is the excitation of only single, say, the kth normal vibration,

$$v_{ki} = v_i, \quad v_{1i} = \ldots v_{k-1,i} = v_{k+1,i} = \cdots = v_{ni} = 0,$$
$$v_{kf} = v_f, \quad v_{1f} = \ldots v_{k-1,f} = v_{k+1,f} = \cdots = v_{nf} = 0.$$

Using the notation $\mathcal{I}_{v_f v_i}(v,k)$ for the corresponding overlap integral, with the help of Refs. [62, Eqs.(20)–(22)] and [65], we obtain (the sum running over all the allowed values)

$$\mathcal{I}_{v_f v_i}(v,k) = \left[\frac{v_f!v_i!}{2^{v_f}2^{v_i}}\right]^{1/2}\mathcal{I}_0 \sum_{f,h,q} \frac{A_{kk}^f B_k^{v_f-q-2f} C_{kk}^h D_k^{v_i-q-2h} E_{kk}^q}{f!(v_f-q-2f)!h!(v_i-q-2h)!q!}, \tag{B8}$$

where

$$\mathcal{I}_0 = [4^n \det(\hat{\Gamma}_f\hat{\Gamma}_i)]^{1/4}[\det(\hat{J}\hat{P})]^{-1/2} \exp\left[-\tfrac{1}{2}\mathbf{K}^\mathsf{T}\hat{\Gamma}_i\mathbf{K} + \tfrac{1}{2}\mathbf{K}^\mathsf{T}\hat{\Gamma}_i\hat{J}\hat{P}^{-1}\hat{J}^\mathsf{T}\hat{\Gamma}_i\mathbf{K}\right], \tag{B9}$$

$$\begin{aligned}
\hat{P} &= \hat{J}^\mathsf{T}\hat{\Gamma}_i\hat{J} + \hat{\Gamma}_f, & \hat{C} &= 2\hat{\Gamma}_f^{1/2}\hat{P}^{-1}\hat{\Gamma}_f^{1/2} - \hat{1},\\
\hat{A} &= 2\hat{\Gamma}_i^{1/2}\hat{J}\hat{P}^{-1}\hat{J}^\mathsf{T}\hat{\Gamma}_i^{1/2} - \hat{1}, & \mathbf{B} &= -2\hat{A}\hat{\Gamma}_i^{1/2}\mathbf{K},\\
\hat{E} &= 4\hat{\Gamma}_f^{1/2}\hat{P}^{-1}\hat{J}^\mathsf{T}\hat{\Gamma}_i^{1/2}, & \mathbf{D} &= -\tfrac{1}{2}\hat{E}\hat{\Gamma}_i^{1/2}\mathbf{K},
\end{aligned}$$

where $\hat{1}$ is a unity $n \times n$ matrix.

In the case of the A_2B molecule, we have $n = 3$ and the numerator k of the normal modes takes the following values: $k = 1$ for the asymmetric stretch normal oscillator (a), $k = 2$ for the symmetric stretch (s), and $k = 3$ for the bending (b) normal oscillators.

The internal coordinates $\mathbf{S}$ in the deformed A_2B molecule are the A–B bond lengths, l_{12} and l_{13}, and the A–B–A bending angle, 2α (see Fig. 1), or $\cos 2\alpha$ which is more convenient to use. By analogy with the $\mathbf{Q}' \equiv \{Q'_a, Q'_s, Q'_b\}$ vector, it is convenient to rename the components of $\mathbf{S} \equiv \{S_1, S_3, S_\alpha\}$.

Then the $\hat{L}_\mu$ matrix ($\mu = i, f$) introduced in Eq. (B3) has dimensions 3×3 for nonlinear molecules of A_2B. Dropping the μ subscript for brevity, we can write out this matrix explicitly:

$$\hat{L} = \begin{bmatrix}
\frac{1}{2\sqrt{M_a}}\left(\frac{2m_A}{m_B}\sin\gamma + \frac{1}{\sin\gamma}\right) & \frac{1}{2\sqrt{M_s}}\left(\sin\gamma + f_s\frac{M}{m_B}\cos\gamma\right) & \frac{1}{2\sqrt{M_b}}\left(\sin\gamma + f_b\frac{M}{m_B}\cos\gamma\right)\\
-\frac{1}{2\sqrt{M_a}}\left(\frac{2m_A}{m_B}\sin\gamma + \frac{1}{\sin\gamma}\right) & \frac{1}{2\sqrt{M_s}}\left(\sin\gamma + f_s\frac{M}{m_B}\cos\gamma\right) & \frac{1}{2\sqrt{M_b}}\left(\sin\gamma + f_b\frac{M}{m_B}\cos\gamma\right)\\
0 & -\frac{\sin 2\gamma}{2l\sqrt{M_s}}\left(\cos\gamma - f_s\frac{M}{m_B}\sin\gamma\right) & -\frac{\sin 2\gamma}{2l\sqrt{M_b}}\left(\cos\gamma - f_b\frac{M}{m_B}\sin\gamma\right)
\end{bmatrix}.$$

The rows of the $\hat{L}$ matrix are enumerated by the "1," "3," and "α" symbols, while its rows are enumerated by "a," "s," and "b". According to Eq. (B7), the vector of the mass-weighted laser-induced displacements of the equilibrium positions of the normal oscillators has the form

$$\mathbf{Q}'_E = \frac{1}{4}F_{0i}F_{0j}\left\{0, \frac{\alpha_{ij}^{(1s)}}{M_s^{1/2}\omega_{0v}^2}, \frac{\alpha_{ij}^{(1b)}}{M_b^{1/2}\omega_{0d}^2}\right\}, \tag{B10}$$

where $\hat{\alpha}^{(1k)}$ matrices were introduced in Sec. IV B. The influence of laser-induced deformation of the molecule on FCFs is accounted for by substituting Eq. (B10) into Eq. (B6).

The $\hat{\Gamma}$ matrix for an A_2B molecule has the simple form

$$\hat{\Gamma} \equiv \mathrm{diag}(\omega_a,\omega_s,\omega_b).$$

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