Enhanced orientation of polar molecules by combined electrostatic and nonresonant induced dipole forces

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Recent experiments have demonstrated the efficacy of orienting low rotational states of a linear polar molecule in a static electric field, $\varepsilon_S$, or aligning a molecule (polar or not) in an intense nonresonant laser field, $\varepsilon_L$. We present theoretical results showing that the combined action of $\varepsilon_S$ and $\varepsilon_L$ can markedly sharpen orientation, particularly by introducing a pseudo-first-order Stark effect for tunneling doublets created by the polarizability interaction. Also, if $\varepsilon_S$ and $\varepsilon_L$ are not collinear, the molecular axis can be localized with respect to $\phi$ as well as $\theta$, since $\hat{M}$ states as well as $J$ states undergo hybridization. Another benefit is a means to eliminate “wrong way orientation” which otherwise occurs for “low-field seeking” states.

For polar molecules in low rotational states, a strong uniform electric field can produce spatially oriented pendular states, in which the molecular axis librates over a limited angular range about the field direction. These directional pendular states comprise coherent superpositions or hybrids of the field-free rotational states $|J, M\rangle$, with a range of $J$ values but fixed values of $M$, which remains a good quantum number by virtue of the azimuthal symmetry about the field. This has proved a convenient means to produce oriented molecules for study of vector correlations in collision processes\textsuperscript{1} and spectra.\textsuperscript{2} It complements a more venerable but less general method, which provides oriented beams in pure rotational states but works only for symmetric top molecules and requires use of long ($\approx 1$ m) inhomogeneous focusing fields.\textsuperscript{3} The hybridization method is applicable to linear and asymmetric tops also and its experimental implementation merely requires installing a short ($\approx 1$ cm) pair of parallel electrodes.\textsuperscript{4}

A kindred version of hybridization, applicable to nonpolar as well as polar molecules, exploits the induced dipole moment resulting from interaction of an intense, nonresonant plane-polarized laser field with the anisotropic molecular polarizability.\textsuperscript{5,6} Since the electric field of the laser rapidly switches direction, its interaction with a permanent dipole averages out. However, the interaction with the polarizability persists, because it is governed by the square of the field strength. The resulting pendular states are aligned (not oriented) with respect to the double-ended electric field. (As usual, here axial anisotropy is designated orientation if it behaves like a single-headed arrow and alignment if it behaves like a double-headed arrow.) As well as its utility for alignment, theoretical work on the polarizability interaction has examined prospects for molecular focusing\textsuperscript{7} and trapping,\textsuperscript{5} rotational spectroscopy of nonpolar molecules,\textsuperscript{8} tunneling splittings arising from the double-ended potential,\textsuperscript{9} alignment enhanced spectra,\textsuperscript{10} and the time evolution of pendular states produced by a pulsed laser.\textsuperscript{11} Recent experiments have demonstrated both strong alignment and focusing of molecular beams by means of the induced dipole force.\textsuperscript{12-14}

Here we show that the orientation of a polar molecule can be enhanced by the combined action of a static field and a nonresonant laser field. If the fields are parallel, the angular amplitude of pendular states is usually narrowed, as a consequence of enhanced hybridization of the $J$ states. For certain pairs of states, which become nearly degenerate tunneling doublets in the laser field,\textsuperscript{9} even a weak static field can induce strong orientation via a pseudo-first-order Stark effect. If the fields are not collinear, $\hat{M}$ states are also hybridized. The orientation of the molecular axis is then no longer azimuthally symmetric about either field. These and other features of the doubly hybridized pendular states offer further useful tools for the control and manipulation of molecular trajectories.

We consider a $^1\Sigma$ molecule, treated as a rigid rotor with a permanent dipole $\mu$ along the internuclear axis and polarizability components $\alpha_\parallel$ and $\alpha_\perp$ parallel and perpendicular to the axis. The angles between the molecular axis and the directions of the static electric field, $\varepsilon_s$, and the electric vector of the plane-polarized laser field, $\varepsilon_L(t)$, are $\theta_S$ and $\theta_L$, respectively. We limit consideration to the adiabatic regime, in which the pulse is turned on and off slowly compared with the rotational periods.\textsuperscript{11,14}

With energies expressed in units of $B$, the Hamiltonian takes the form

$$H = \mathbf{J}^2 + V_\mu(\omega; \theta_S) + V_\alpha(\omega_\parallel, \omega_\perp; \theta_L)$$  \hspace{1cm} (1)

where $\mathbf{J}^2$ is the squared angular momentum operator. The interaction potentials are
\[ V_{\mu}(\omega; \theta_3) = -\omega \cos \theta_3, \]
\[ V_{\mu}(\omega \parallel, \omega \perp; \theta_L) = - (\Delta \omega \cos^2 \theta_L + \omega \perp), \]
with dimensionless parameters defined by
\[ \omega = \frac{\mu \varepsilon_S}{B}; \quad \Delta \omega = \omega \parallel - \omega \perp; \quad \omega \perp = \frac{\alpha \perp I_L}{2B}, \]
where \( I_L(t) = \langle \varepsilon_S^2(t) \rangle \) is the laser intensity profile after averaging over the oscillating time dependence. With quantities expressed in customary practical units
\[ \omega = 0.0168 \mu(D) \varepsilon_S (kV/cm)/B(cm^{-1}), \]
\[ \Delta \omega = 10^{-11} \Delta \alpha (\text{Å}^3) I_L(W/cm^2)/B(cm^{-1}). \]
For example, for the ground state of the ICl molecule, \( B = 0.114 \text{ cm}^{-1} \), \( \mu = 1.24 \text{ D} \), \( \Delta \alpha = \alpha \perp = 9 \text{ Å}^3 \). Thus, for \( \varepsilon_S = 30 \text{ kV/cm} \), and \( I_L = 10^{12} \text{ W/cm}^2 \), we have \( \omega = 5.5; \Delta \omega \approx \omega \perp \approx 780 \). In this case, \( h/B = 0.05 \text{ ns} \), so adiabatic behavior is readily attained using pulse rise times of a few ns.

In evaluating eigenproperties, as in previous treatments dealing with either \( \varepsilon_S \) or \( \varepsilon_L(t) \) alone, it is natural and efficient to set up secular equations by expanding the wave functions in spherical harmonics, \( Y_{J'M'}(\theta, \phi) \), the field-free eigenfunctions. If the tilt angle \( \beta \) between the field directions is nonzero, the relation
\[ \cos \theta_3 = \cos \beta \cos \theta + \sin \beta \sin \theta \cos \phi, \]
is employed, with \( \theta, \phi = \theta_L, \phi_L \). The pendular eigenfunctions
\[ \psi = \sum_{J,M} \langle \tilde{J}, \tilde{M}; \beta, \omega, \Delta \omega \rangle Y_{J'M'}(\theta, \phi) = |\tilde{J}, \tilde{M} \rangle \langle \beta, \omega, \Delta \omega \rangle, \]
and hybridization coefficients, \( c_{J'M'}(\beta, \omega, \Delta \omega) \), are labeled with nominal \( J, M \) symbols which designate the values of \( J \) and \( M \) for the field-free rotor state that adiabatically correlates with the hybrid state. The range of \( J \) and \( M \) that contribute to this coherent superposition increases with the \( \omega \) and \( \Delta \omega \) parameters. If the fields are collinear (\( \beta=0^\circ \)), however, the sum extends over \( J \) only, with \( \tilde{M} = M \) fixed.

For the nine states with \( \tilde{J}, \tilde{M} \leq 2 \), we evaluated as functions of \( \beta, \omega, \) and \( \Delta \omega \) the eigenenergies, hybridization coefficients, and expectation values of quantities characterizing the extent of orientation and alignment: \( \langle \cos \theta_3 \rangle, \langle \cos^2 \theta_3 \rangle \), and \( \langle \cos \phi_3 \rangle \). To illustrate typical features, we consider here results when the fields are either collinear or perpendicular, chiefly for the two states with \( \tilde{J}, \tilde{M} = 0,0 \) and \( 2,0 \). In a static field alone, these states exhibit “high-field seeking” and “low-field seeking” behavior, respectively. For the 0,0 state, since the interaction of the molecular dipole with the field is purely attractive, \( \langle \cos \theta_3 \rangle \) is always positive and monotonically increasing with the field strength. For the 2,0 state, however, the net interaction is initially repulsive and \( \langle \cos \theta_3 \rangle \) remains negative until the field becomes rather strong (\( \omega > 14 \)). Such “wrong-way” orientation occurs for any state in which the dipole continues to wobble, with its plane near the field direction, since then the dipole speeds up as it swings toward the field and slows down as it retreats.

Figure 1 displays results for collinear static and laser fields. As the fields cooperate in inducing hybridization, the general effect is to narrow the angular width of the pendular states. For the 0,0 state, \( \langle \cos \theta_3 \rangle \) for a given \( \omega \) simply grows steadily larger as \( \Delta \omega \) is increased. Likewise, \( \langle \cos^2 \theta_3 \rangle \) for a given \( \Delta \omega \) grows as \( \omega \) is increased. The 2,0 state exhibits more specific effects of the enhanced hybridization. When \( \omega \) is small, turning on a sizable \( \Delta \omega \) can switch \( \langle \cos \theta_3 \rangle \) from negative to positive, but as \( \omega \) is increased, \( \langle \cos \theta_3 \rangle \) becomes negative again before it eventually grows steadily positive. Nonmonotonic variations also occur in \( \langle \cos^2 \theta_3 \rangle \), at values of the field parameters that are not large enough to bind the state in the combined potential well. In this regime, the 2,0 state exhibits one such term as “wrong-way alignment,” in which the molecular axis points predominantly perpendicular to the laser field.

However, the permanent and induced dipole potentials also compete with one another, even if the fields are collinear. This arises because the hierarchy of the respective energy levels is different (for a given \( \tilde{J} \), levels with larger \( M \) have lower energy for the permanent dipole interaction and higher energy for the induced dipole interaction). Moreover, states hybridized by the permanent dipole interaction differ by \( \Delta J = \pm 1 \), whereas those mixed by the polarizability interaction differ by \( \Delta J = \pm 2 \). Thus, particularly for low \( J \) states coupled to neighbors lying both below and above them in energy, the resultant dependence on \( \omega \) and \( \Delta \omega \) can become wobbly.

Figure 2 illustrates another consequence of the distinct
character of the two varieties of hybridization, of special interest and potential utility. Because the polarizability interaction, proportional to $\cos^2 u_L$, has end-for-end symmetry, its low-lying pendular levels occur as pairs. The lowest such pair correlates with the 1,0 and 0,0 levels of the field-free molecule. For large $Dv$, these levels split apart strongly and thus acquire large effective dipole moments, opposite in sign. Thereby the molecular axis becomes oriented, in the 0,0 state parallel to $\epsilon_S$, in the 1,0 state antiparallel.

When the fields are not collinear, the hybridization process runs rife. As well as mixing $M$-states, the introduction of azimuthal asymmetry makes energy levels that differ in the sign of $M$ no longer degenerate. Also, as $\omega$ and $\Delta \omega$ vary, various pairs of $J, M$ levels often intersect; these are genuine crossings rather than avoided crossings. Figure 3 shows for $\beta=90^\circ$ results corresponding to those in Fig. 1 for $\beta=0^\circ$. For ease of comparison with the field-free limits, when considering orientation we take $M=M_\perp$, but when considering alignment take $M=M_\parallel$. With perpendicular fields, states with a given $J$ and $M_S=0$ involve averaging over states with $M_\perp$ ranging from 0 to $J$ and vice versa. Rather than cooperating in augmenting the hybridization along a common direction, as in Fig. 1, the perpendicular fields are competing, each trying to have the pendular dipole favor a direction orthogonal to the other field.
Accordingly, in Fig. 3 for the 0,0 state the orientation \(\langle \cos \theta_u \rangle\) for a given \(\omega\) weakens steadily (rather than strengthens as in Fig. 1) when \(\Delta \omega\) is increased. Likewise, for 0,0 the alignment \(\langle \cos^2 \theta_u \rangle\) for a given \(\omega\) decreases as \(\Delta \omega\) is increased. However, for the 2,0 state the competition of the orthogonal fields turns out to offer a useful means of suppressing the “wrong-way” orientation that occurs for low-field seeking states. As seen in Fig. 3, for such a state with \(\langle \cos \theta_u \rangle\) negative in a static field, even when \(\omega\) remains small the orientation can be made positive by subjecting the molecule to a substantial \(\Delta \omega\) delivered by an orthogonal laser field. For sufficiently large \(\Delta \omega\), a positive \(\langle \cos \theta_u \rangle\) is attained for all \(\omega\), ensuring right-way orientation. This occurs for the 2,0 state when \(\Delta \omega > 9\) and for all \(\tilde{J} \approx \tilde{M}\) states with \(\tilde{J} \approx 2\) when \(\Delta \omega > 17\). Similar results should often be attainable for higher \(\tilde{J}\) states also, since much larger values of \(\Delta \omega\) are feasible for many molecules. Currently, uncertainties imposed by the presence of states with \(\langle \cos \theta_u \rangle\) negative have handicapped interpretation of experiments employing a static field alone to produce oriented pendular molecules.\(^{15,16}\)

The competition between noncollinear fields also ensures that the azimuthal angles, \(\phi_3\) and \(\phi_L\), of the molecular axis will not be uniformly distributed about either field. For \(0^\circ < \beta < 90^\circ\) (\(C_3\) symmetry), the only general constraint is that the molecular axis be distributed symmetrically with respect to the plane defined by the field vectors. For \(\beta = 90^\circ\) (\(C_{2v}\) symmetry), the axis distribution must also be symmetric with respect to a 180° rotation about the \(e_S\) vector.

The technique of aligning or focusing neutral molecules by means of an intense nonresonant nanosecond laser pulse has many prospective applications.\(^{5,9-16}\) As indicated by the analysis given here, all of these can be enhanced, for polar molecules, by merely adding a static field. This field need extend only over the focal volume of the laser beam, so the experimental implementation is easy. Particularly inviting is the opportunity to exploit the pseudo-first-order Stark effect illustrated in Fig. 2. This is not limited to linear molecules, but can be induced whenever anisotropy of the polarizability tensor creates an angular double-well potential. For instance, the exceptionally strong orientation produced by the pseudo-first-order interaction may enable state-selection of the 0,0 and 1,0 pendular states, filtering them out from all the other much less strongly oriented states. A major limitation is that the orientation persists only for the duration of the pulse. Yet a nanosecond pulse is amply long to enable pico- or femtosecond experiments with the oriented molecules.

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\(^{3}\)P. R. Brooks, J. Phys. Chem. 97, 2153 (1993), and work cited therein.