Alignment and Trapping of Molecules in Intense Laser Fields

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(Received 12 December 1994)

The anisotropic interaction of the electric field vector of intense laser radiation with the dipole moment *induced* in a *polarizable* molecule by the laser field creates aligned pendular states. These are directional superpositions of field-free states, corresponding to oblate spheroidal wave functions, with eigenenergies that decrease with increasing field strength. We present calculations demonstrating the utility of these states for both laser alignment and spatial trapping of molecules.

PACS numbers: 33.20.–t, 33.15.–e, 33.55.–b, 33.80.–b

A recent experiment of Normand, Lompre, and Cornaggia [1] provides evidence that a strong pulsed laser field ($I \sim 10^{14}$ W/cm^2, pulse duration between 1 and 30 ps) can create alignment of a thermal ensemble of CO molecules, *prior* to their dissociative ionization. Here we propose a mechanism to account for this molecular alignment; it is governed by the interaction of the electric field vector of the radiation with the anisotropy of the molecular polarizability. The anisotropy arises from the *induced* dipole moment and creates *pendular* eigenstates, directional hybrids of the field-free rotational states, in which the molecular axis librates about the electric field vector. We show that the CO alignment [1] involves hybridization strong enough to bring the eigenproperties close to the harmonic librator limit. For instance, the energy of the ground pendular state drops below the $J = 0$ field-free level by about 0.5 eV, and the angular amplitude of this state is only $\pm 10°$.

Furthermore, we find that the polarizability interaction, combined with buffer-gas loading [2], also offers a means to attain spatial trapping of molecules in a fashion similar to the far-off-resonance technique for atoms [3]. Supermirror technology [4] enables cw laser intensities above 10^{10} W/cm^2 within a small trap volume of about 10^{-9} cm^3 at the waist of a focused infrared beam. For a fairly polarizable molecule, such as CS_2, the ground pendular state in this region corresponds to a well depth exceeding 600 mK. This is appreciably deeper than the minimum temperature of 240 mK required for buffer gas (^{3}He) loading of a trap [2].

The prospect of enhancing dynamical resolution of collisional or spectroscopic experiments has motivated recent work on pendular orientation or alignment of molecules, produced by static electric [5] or magnetic fields [6] acting on *permanent* dipole moments. However, since all molecules (and atoms) are polarizable, the potential scope is much greater for pendular alignment and trapping in intense laser fields by means of *induced* dipole moments.

For simplicity, we consider a linear rotor subject to radiation with electric field strength $\varepsilon = \varepsilon_0 \cos(2\pi\nu t)$. The Schrödinger equation is

$$[B\mathbf{J}^2 + V_\mu(\theta) + V_\alpha(\theta)]\Psi = E\Psi\,, \tag{1}$$

with $\mathbf{J}^2$ the squared angular momentum operator, B the rotational constant, E the eigenenergy, and θ the polar angle between the molecular axis and the electric field direction. For a permanent dipole moment μ along the internuclear axis and polarizability components $\alpha_\parallel$ and $\alpha_\perp$ parallel and perpendicular to the axis, the interaction potentials are

$$V_\mu(\theta) = -\mu\varepsilon\cos\theta\,, \tag{2a}$$

$$V_\alpha(\theta) = -\tfrac{1}{2}\varepsilon^2(\alpha_\parallel\cos^2\theta + \alpha_\perp\sin^2\theta)\,. \tag{2b}$$

For nonresonant frequencies much greater then the reciprocal of the laser pulse duration, $\nu \gg \tau_p^{-1}$, averaging over the pulse period τ_p quenches the V_μ interaction and converts ε^2 in V_α to $\varepsilon_0^2/2$. When $\alpha_\parallel > \alpha_\perp$, which always holds for linear molecules, the time average of Eq. (1) reduces to an oblate spheroidal wave equation

$$\left[\frac{d}{dz}\left[(1-z^2)\frac{d}{dz}\right] - \frac{M^2}{1-z^2} + \lambda_{\tilde{J},M} + c^2z^2\right]S_{\tilde{J},M} = 0\,, \tag{3}$$

where $z = \cos\theta$. The eigenvalues $\lambda_{\tilde{J},M}$ and eigenfunctions $S_{\tilde{J},M}$ can be obtained from extensive tabulations or computed with arbitrary accuracy by standard methods [7,8]. In terms of dimensionless interaction parameters [9],

$$\omega_{\parallel,\perp} \equiv [\alpha_{\parallel,\perp}\varepsilon_0^2/4B]\,, \tag{4}$$

$$c^2 \equiv \Delta\omega = \omega_\parallel - \omega_\perp\,, \tag{5}$$

and

$$\lambda_{\tilde{J},M} = \omega_\perp + E_{\tilde{J},M}/B\,. \tag{6}$$

For $\Delta\omega = 0$, the eigenproperties become those of a field-free rotor; the eigenfunctions then coincide with spherical harmonics, and the eigenvalues become $\lambda_{\tilde{J},M} \to E_{J,M}/B = J(J+1)$. The eigenstates can thus be labeled by $|M|$ and the nominal value of $\tilde{J}$ of the angular momentum for the field-free rotor state that adiabatically correlates with the high-field hybrid function.

Table I gives the leading terms in perturbation expansions of the eigenenergy $E_{\tilde{J},|M|}/B$, applicable when $\Delta\omega$ is small or large, corresponding to the low- and high-field

0031-9007/95/74(23)/4623(4)$06.00

limits. Also given are limiting results for $\langle\cos^2\theta\rangle_{\tilde{J},|M|}$, which characterizes the extent of alignment. In the high-field limit $\Delta\omega \to \infty$ the range of θ is confined near zero, and Eq. (3) reduces to that for a two-dimensional angular harmonic librator. Note that states with $\tilde{J} = N + 1$ for $\tilde{J} - |M|$ odd and $\tilde{J} = |N|$ for $\tilde{J} - |M|$ even, with the same $N = 2(k + |M|/2)$ and $k = 0, 1, 2\ldots$, have equal energies in the harmonic librator limit.

Figure 1 shows the interaction potential $-\omega_\perp - \Delta\omega\cos^2\theta$, the energy levels, and the spheroidal wave functions $S_{\tilde{J},M}$ for $\alpha_\parallel/\alpha_\perp = 2$ and $\Delta\omega = 3$. The potential is purely attractive. The anisotropic part governed by $\Delta\omega$ produces a double well corresponding to the end-for-end symmetry. The hybrid pendular states bound by these wells hence occur in pairs, split by tunneling (e.g., the $\tilde{J}_{|M|} = 0_0$ and 1_0 pair). The amplitude of the wells and thus the number of bound states increases with $\Delta\omega$, so it grows quadratically with field strength. For even $|M|$, the eigenfunctions in the two wells are in-phase reflections of one another; for odd $|M|$, out-of-phase reflections. The correlations with the field-free rotor states $J_{|M|}$ and the harmonic librator states $N_{|M|}$ are also indicated.

The expectation value of the squared alignment cosine is readily evaluated from the Hellman-Feynman theorem [10], and the ensemble average is given by

$$\langle\cos^2\theta\rangle = \sum_{\tilde{J}} w_{\tilde{J}} \sum_{M=-\tilde{J}}^{M=+\tilde{J}} \langle\cos^2\theta\rangle_{\tilde{J},M}\,, \qquad (7)$$

where $w_{\tilde{J}} = \exp[-\tilde{J}(\tilde{J}+1)/\Upsilon]/Q_r$, with Q_r the rotational partition function and $\Upsilon \equiv kT/B$ the reduced rotational temperature. This determines the second Legendre moment

$$b_2(\Delta\omega, \Upsilon) \equiv 5\langle P_2(\cos\theta)\rangle = \tfrac{5}{2}\,(3\langle\cos^2\theta\rangle - 1)\,. \qquad (8)$$

The customary expansion of the alignment angular distribution, $n(\theta) = 1 + b_2 P_2(\cos\theta) + \cdots$ is awkward for large $\Delta\omega$ as higher terms become substantial. However, a Gaussian form [11] provides a good approximation $n(\theta) = \exp(-\frac{1}{2}\sin^2\theta/\sigma^2)$, with the variance given by $\sigma^2 = 1 - \langle\cos^2\theta\rangle$. Figure 2 enables quick estimates of b_2 or $\langle\cos^2\theta\rangle$ and hence the ensemble alignment in terms of the rotational temperature, polarizability, rotational constant, and laser intensity.

Spectra of pendular states produced by the polarizability interaction are distinctive. Since the hybrid states are of definite parity (positive for $\tilde{J}$ even and negative for $\tilde{J}$ odd), electric dipole transitions can occur only between states with different parities. However, there are nonzero transition probabilities between states that differ by more than unity in their nominal $\tilde{J}$ values, increasingly as $\Delta\omega$ increases. The selection rule for electric dipole transitions between pendular states thus is $\Delta\tilde{J} \equiv \tilde{J}' - \tilde{J}'' = \pm1, \pm3, \pm5, \ldots$. The selection rules for the good quantum number M reflect the polarization of the probe laser with respect to the direction of the hybridizing field and remain $\Delta M = 0, \pm1$, the same as in Stark or Zeeman spectroscopy. The field dependence of the frequency of a given transition can be used [10] to evaluate the molecular-axis alignment of the states involved in the transition.

The Saclay experiment [1] employed an elegant double-pulse technique to establish that CO molecules are aligned along the polarization vector before dissociation. The alignment is exhibited by the angular distributions measured for fragment atomic ions from six channels for dissociation of CO^{+q} molecule ions ($q = 1, 2, 3$), which are produced by sequential absorption of 12 or more infrared photons. The observed half widths of the fragment ion distributions varied from 55° for slow ions from CO^+ formed at the lowest threshold laser intensity ($\sim 5 \times 10^{13}$ W/cm^2) to 18° for fast ions from CO^{+3} formed at the highest threshold laser intensity ($\sim 6 \times 10^{14}$ W/cm^2). A quantitative evaluation is precluded, however. The

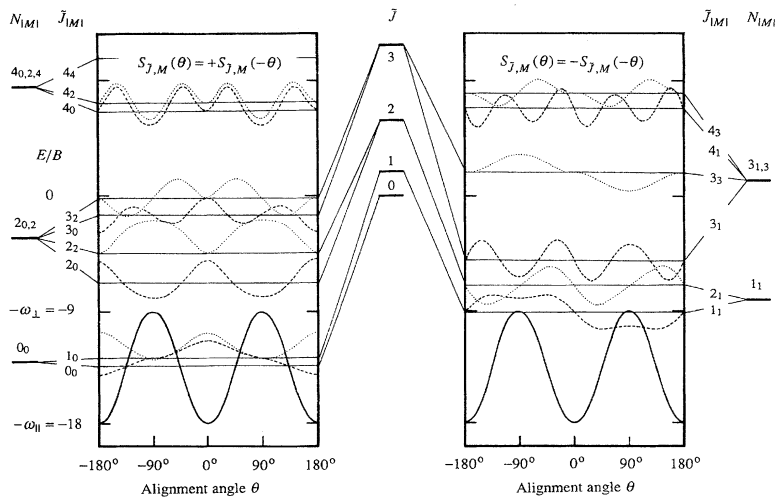

FIG. 1. Patterns of pendular energy levels and spheroidal wave functions, correlated with field-free rotational states. The eigenfunctions are symmetric or antisymmetric to $\theta \to -\theta$ (equivalent to $\phi \to \pi - \phi$) for even or odd values of the M quantum number. At the minima of the time-averaged interaction potential: $\overline{V}(0°) = \omega_\parallel$ and $\overline{V}(180°) = \omega_\perp$. See text.

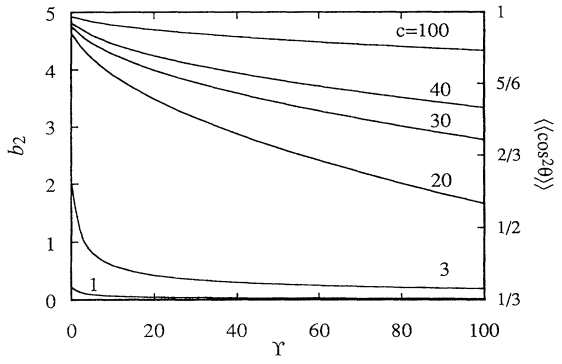

FIG. 2. Dependence of ensemble-averaged alignment parameters b_2 and $\langle\cos^2\theta\rangle$ of Eq. (8) on anisotropy parameter $c = (\Delta\omega)^{1/2}$ of Eq. (5) and reduced rotational temperature $\gamma \equiv kT/B$.

reduced temperature $\Upsilon = 110$, but the interaction parameters $\Delta\omega$ for the various decay channels can only be roughly estimated. These channels occur in different spatial regions of the focused laser beam, among which the local field intensity varies by perhaps approximately tenfold or more and is only roughly known. Also, since the multiphoton excitation occurs in a time short compared to the laser pulse duration, the polarizability anisotropy that governs the alignment may be substantially larger than that for the ground electronic state. A nominal $\Delta\omega = 1600$ for the ground state polarizability and rotational constant when $I = 6 \times 10^{14}$ W/cm^2.

Figure 3 shows alignment angular distributions computed for a range of $\Delta\omega$ and Υ values. At high $\Delta\omega$ the alignment becomes quite sharp unless Υ is very high, because hybridization is strong for most states even in a warm ensemble. Likewise, at low Υ the alignment sharpens unless $\Delta\omega$ is also low because mainly the lower, more hybridized states contribute. For $\Upsilon = 110$, we find the alignment half width, obtained simply from $\sin^2\theta_{1/2} = (2\ln 2)\sigma^2$, varies from 19° for $\Delta\omega = 4000$ to 53° for $\Delta\omega = 400$. This is at least consistent with the Saclay data and kindred results [12]. A much more incisive test could be obtained from spectra of the aligned molecules at field strengths too low for dissociative ionization.

The possibility of trapping molecules by means of the polarizability interaction is inviting, since the various traps thus far developed for atoms [13] are not applicable to un-ionized molecules. The pendular eigenenergies for the purely attractive V_α potential of Eq. (2) decrease with the field strength; thus, in an inhomogeneous field, molecules in such pendular states seek regions of maximum field strength. As demonstrated by the far-off-resonance technique for atom trapping [3], the Gaussian intensity profile of a TEM_{00} laser mode provides a suitable inhomogeneous field. Although a pulsed laser operating at high repetition rates $\sim 10^0$ kHz could be used for trapping, a cw laser is preferable. Available cw infrared lasers can deliver up to a few kW, and by focusing to a beam waist of 10 μm diameter by means of high-finesse cavities [4], it is possible to increase the power by about a factor of 50. Within a roughly spherical trapping volume of about 10^{-9} cm^3, the maximum laser field would then exceed 10^{11} W/cm^2, sufficient to provide a well depth of the order of 1 K or more for typical molecular polarizabilities.

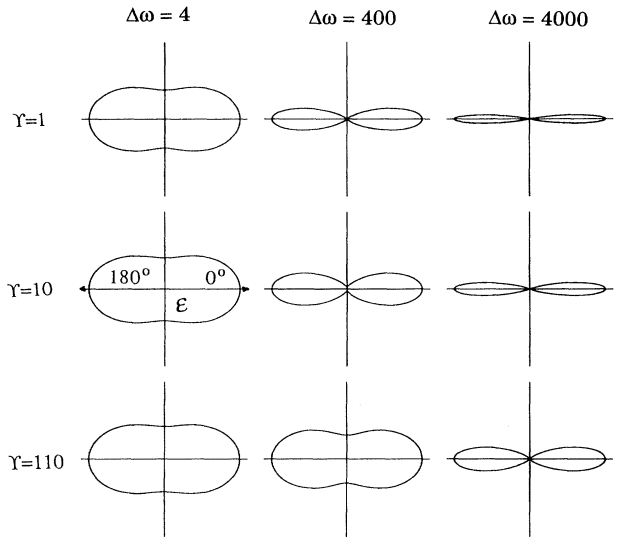

FIG. 3. Polar plots of ensemble-averaged alignment angular distributions (Gaussian form) for $\Delta\omega = 4$, 400, and 4000 and $\gamma = 1$, 10, and 110.

The technique of buffer-gas loading [2] appears well suited for filling such a pendular state trap. This relies on dissipating the molecular translational and rotational energy by collisions with cold ^{3}He buffer gas, maintained

TABLE I. Limiting values of eigenenergy, $E_{\tilde{J},M}/B$, and alignment cosine, $\langle\cos^2\theta\rangle$; $c^2 = \Delta\omega \equiv \omega_\parallel - \omega_\perp$ with $\omega_{\parallel,\perp} \equiv [\alpha_{\parallel,\perp}\varepsilon_0^2/4B]$.

	$E_{\tilde{J},M}/B$	$\langle\cos^2\theta\rangle$
Low field: $c \to 0$	$\tilde{J}(\tilde{J}+1) - \frac{c^2}{2}\left[1 - \frac{(2\lvert M\rvert-1)(2\lvert M\rvert+1)}{(2\tilde{J}-1)(2\tilde{J}+3)}\right] - \omega_\perp$	$\frac{1}{2}\left[1 - \frac{(2\lvert M\rvert-1)(2\lvert M\rvert+1)}{(2J-1)(2J+3)}\right] + c^2\left[\frac{(J-\lvert M\rvert+1)(J-\lvert M\rvert+2)(J+\lvert M\rvert+1)(J+\lvert M\rvert+2)}{2(2J+1)(2J+3)^3(2J+5)}\right]$
High field: $c \to \infty$	$-c^2 - \omega_\perp + 2c + 2c\tilde{J} + \lvert M\rvert^2/2 - \tilde{J}^2/2 - \tilde{J} - 1$	$1 - (\tilde{J}+1)/c$ for $(\tilde{J} - \lvert M\rvert)$ even
	$-c^2 - \omega_\perp + 2c\tilde{J} + \lvert M\rvert^2/2 - \tilde{J}^2/2 - 1$	$1 - \tilde{J}/c$ for $(\tilde{J} - \lvert M\rvert)$ odd

TABLE II. Expected trap depths and number densities of trapped molecules and their alignment. Based on polarizabilities and rotational constants of Refs. [16,17], eigenproperties of Table I and buffer-gas loading parameters of Ref. [2]. The number density n_0 of the trapped molecules is derived in the usual way [2,3] from the well depth and a steady flow of 10^{12} molecules/s into the loading buffer-gas volume, without recourse to evaporative cooling.

Molecule	Laser intensity [W/cm^2]	Buffer-gas temperature [K]	$E_{0,0}/k$ [K]	n_0 [cm^{-3}]	$\langle\cos^2\theta\rangle$
CO	5×10^{10}	0.24	0.7	4×10^8	0.34
	1×10^{11}	0.24	1.4	6×10^9	0.35
	1×10^{11}	1	1.4	4×10^7	0.35
CS_2	1×10^{10}	0.24	0.6	2×10^8	0.52
	5×10^{10}	0.24	4.1	6×10^{14}	0.79
	1×10^{11}	1	9.0	7×10^{10}	0.85
C_{60}	1×10^{10}	1	6	1×10^{10}	1/3
	1×10^{11}	4	60	4×10^{13}	1/3

by a dilution refrigerator or other cryogenic device. At or above 240 mK the vapor pressure of ^{3}He exceeds 5×10^{15} cm^{-3}, adequate for collisional relaxation. Molecules entering the trap volume, if sufficiently cooled, will "sink" into the conservative potential of the trap, determined by the eigenenergy of the given pendular state.

Advantageous features of this scheme include: (1) For the polarizability interaction, all molecular field-free rotational states correlate with high-field seeking pendular states; neither the trapping nor the loading depends on any particular energy level pattern. (2) At the low temperature of the buffer gas, most linear molecules have $Y \leq 1$, so essentially only the ground rotational state (i.e., $J = 0$ for most molecules) would be populated; this correlates with the pendular ground state. An ensemble of molecules trapped via the pendular ground state would thus lack a collisional loss mechanism since that state cannot decay. This fosters the accumulation of molecules in the trap. (3) Trapped molecules, thereby, can be concentrated at number densities sufficient to allow collisional equilibration. Evaporative cooling [14] of the trapped ensemble then becomes feasible. Lowering the trap depth by decreasing the laser intensity would release the highest-energy molecules from the trap. Subsequent rethermalization of the rest (after removing the ^{3}He buffer gas) would then drop the temperature. In principle, by interaction the trap temperature could be lowered below the photon recoil limit [15].

Table II lists nominal trap depths, densities, and alignments for three representative molecules, CO, CS_2, and C_{60}, with polarizability small, fairly large, and very large, respectively. The trap populations depend exponentially on both the trap depth and buffer-gas temperature, but compare favorably with those achieved for atoms [3].

We thank Professor John Doyle (Harvard University) for discussions of buffer-gas loading and evaporative cooling. Financial support of the National Science Foundation is gratefully acknowledged.

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