Design of tailored microwave pulses to create rotational coherent states for an asymmetric-top molecule

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Tailored microwave pulses, to guide asymmetric-top molecules from selected rotational states belonging to the vibronic ground state to generalized angular-momentum coherent states, are designed by using optimal control theory. Characteristics that the molecules have to fulfill in order to achieve the goal with feasible pulses are discussed. Properties of the pulses are discussed as well. The further dephasing among the components of the wave packet which, for the simplest coherent state, is a form of dynamical tunneling, can be locked by exploiting the changes that energy levels and eigenfunctions undergo in the presence of an external static electric field with appropriate intensity. For the special case with $M = 0$, periodic fields are more flexible in avoiding dephasing. This is shown by examining properties of quasienergies and dressed states resulting from the diagonalization of a truncated Floquet matrix. [S1050-2947(98)03006-6]

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I. INTRODUCTION

Coherent states are quantum states with a strong classical character. They were proposed originally for the harmonic oscillator by Schrödinger [1], although the term ''coherent state'' was introduced by Glauber [2] in quantum optics. In the harmonic oscillator, due to the fact that the energy levels are equally spaced, coherent states do not spread, and the expectation values for coordinate and momentum are solutions of Hamilton's equations at any time. Since Glauber's work, a number of coherent states with different properties have been proposed from a theoretical point of view for different systems: squeezed states [3], atomic coherent states [4], intelligent states [5], angular-momentum coherent states [6–8], wave packets for Rydberg atoms (Trojan states [9], elliptical squeezed states [10]), etc. Usually three different definitions are given for generalized coherent states of arbitrary dynamical systems: (i) eigenstates of the lowering operator, (ii) states of minimum uncertainty, and (iii) displaced states of a reference state. A critical comparison of the three approaches and group-theoretical algorithms to build coherent states can be found in the excellent review paper of Ref. [11].

The experimental realization of generalized coherent states has begun to be studied with the same interest. Some papers dealing with coherent states for Rydberg electrons in atoms [12], coherent states for photons [13], SU(1,1) intelligent states [14], and vibrational wave packets for anharmonic molecules [15] have been published. Since these objects are a bridge between the classical and quantum worlds, their experimental study should be illuminating.

In the present paper the possibility of creating generalized angular momentum coherent states (AMCS's) for asymmetric top molecules by using tailored microwave radiation is investigated. For this kind of state (as for coherent states of any compact group), definition (i) is not appropriate [16]. AMCS's are defined properly by generalizing definition (iii). Our goal is the design of microwave fields able to create AMCS's for a rigid or semirigid [17] asymmetric top molecule by using optimal control theory. The different energy of the states forming the coherent wave packet gives rise to dephasings that destroy the localization, and minimum uncertainty properties which are characteristic of the coherent state. The introduction of further static electric fields can cancel the dephasing for the simplest coherent state. Periodic fields can also produce the same effect, as can be shown by examining quasienergy plots obtained by diagonalizing the appropriate Floquet Hamiltonian [18]. For the simplest AMCS (an extremal state, given by the symmetric-top eigenfunction $|J,k=-J\rangle$, where J is the angular momentum and k is its projection onto the molecule-fixed z axis), the dephasing is equivalent to dynamical tunneling between $+K$ and $-K$ (K is the absolute value of k) regions of the classical phase space. Therefore, the application of appropriate fields can be understood as a form of tunneling suppression, although its mechanism is essentially different from a related phenomenon discovered for quartic double wells [19–21].

Research in the field of coherent control of molecular states has mainly been dedicated to the design of shaped laser pulses to control vibrational wave packets [22] or branching ratios of chemical reactions [23]. However, only a few papers on coherent control of rotational states have been published [24–26]. Hudson *et al.* [24] discussed the capabilities of microwave pulses to create superpositions of rotational eigenfunctions for diatomic molecules with a high degree of orientation, and the design of pulses with reasonable microwave peak power to achieve maximum population transfer at specific target times. Oriented states of molecules with small dipole moments can be created with these techniques, in contrast to the pendular states created by the brute force method [27], which is only feasible for molecules with a high value of the ratio between the dipole moment and the rotational constant (μ/B). However, the oriented states created by a microwave pulse remain oriented for only a very short time after the pulse ends due to dephasing among components, and consequently their usefulness is much more limited than that of genuine pendular states, which are eigenfunctions of a time-independent molecule-field Hamiltonian with trivial time evolution.

The creation of coherent rotational states for nuclei and molecules by using strong nonresonant electromagnetic pulses was suggested in Ref. [25]. For molecules, the rotational coherent states are created via Raman-scattering processes that can generate superpositions of about 40 rotational states. The phenomenon was described in Ref. [25] using, in the sudden approximation, quantum field-theoretical methods for the electromagnetic field. The method is especially appropriate to create coherent states for diatomic and linear molecules with no permanent dipole moment since the molecule-field interaction takes place through the dipole induced by the field (polarizability). A close idea was further explored by Friedrich and Hersbach [28], who studied the creation of pendular states (directional superpositions of field-free rotor states) of diatomic molecules by using strong short nonresonant lasers. The rotational coherent states studied in the present paper are superpositions of field-free asymmetric-top eigenstates with fixed J, and therefore they cannot be created with the method proposed in Ref. [25] because the Raman-type transitions would also populate states with different J values. However, it would be worth exploring its use for the creation of the oscillatorlike states of Gulshani [8]. Other studies related to rotational coherence phenomena were undertaken by Siederman [26], who studied the possibility of aligning linear and symmetric-top molecules by using a laser of moderate intensity resonant with an electronic transition. This laser can create rotational wave packets well defined in the conjugate angle space, but with a broad distribution in angular momentum space. On the other hand, Felker, Baskin, and Zewail [29] studied the consequences of free rotation in molecules excited by short laser pulses.

Our approach uses Krotov's method [30,31] for solving optimal control theory problems, as formulated originally by Rice and co-workers [32,33], and more formally by Rabitz and co-workers [34]. Our problem can be stated in the following form: find a field that guides a pure initial state to a specific target (rotational coherent state) after a predetermined time subject to a constraint in the power of the microwave field.

In Sec. II, angular momentum coherent states for asymmetric top molecules are discussed. In Sec. III, the algorithms employed to determine optimal fields for this particular problem are revised, and the results for a model molecule are discussed. In Sec. IV, the use of further static and periodic fields to avoid dephasing and destruction of the coherent state is discussed. Finally, some theoretical questions and ideas that could be answered by the experimental study of rotational coherent states are discussed in Sec. V.

II. ANGULAR-MOMENTUM COHERENT STATES FOR ASYMMETRIC-TOP MOLECULES

The rotational Hamiltonian of an asymmetric-top molecule in the electronic-vibrational ground state can be written as

$$H_0 = AJ_a^2 + BJ_b^2 + CJ_c^2, \qquad (2.1)$$

where J_a, J_b, and J_c are the components of the angular momentum along molecule-fixed principal axes of inertia a, b, and c, and A, B, and C (with $A > B > C$) are the rotational

constants which are basically the inverse of the moments of inertia. Eigenvalues and eigenvectors of this Hamiltonian can be obtained by diagonalizing a matrix representation of H_0 in a basis set of symmetric-top wave functions $|J,k,M\rangle$, where M is the projection of $\mathbf{J}$ onto the laboratory-fixed Z axis, and k is the projection of $\mathbf{J}$ onto the molecule-fixed a axis. For the rotational eigenstates of the asymmetric top, M is a good quantum number, but k is not. Therefore, the rotational eigenstates of asymmetric tops are commonly labeled by the rigurous quantum numbers J and M, and by the approximate quantum numbers K_a and K_c, which indicate, respectively, the prolate symmetric-top and oblate symmetric-top levels with which the particular asymmetric-top energy level is correlated [35]. These two labels are assigned unambiguously from the energy ordering in such a way that K_a varies from zero (for the lowest state of a given J) to J (for the highest state), and K_c from J to zero. Therefore, the rotational wave functions of the asymmetric top are represented by the ket $|J,K_a,K_c,M\rangle$, and the energy levels are labeled by J_{K_a,K_c}.

The Lie group appropriate for this problem is SU(2). Coherent states for this group are defined for a fixed value of the total angular momentum J. They can be generated by displacing a minimum uncertainty state belonging to the Hilbert space spanned by the basis $|J,k\rangle$, $k=-J,\ldots,J$. The unitary operator which carries out the displacement of the reference state $(|J,k=-J\rangle)$ is [36]

$$U(\theta,\phi) = \exp(\xi J_+ - \xi^* J_-), \qquad (2.2)$$

where $J_\pm = J_x \mp J_y$, and $\xi = (\theta/2)e^{-i\phi}$. The coordinates θ and ϕ are the polar and azimuthal angles which parametrize the classical phase space for this problem (the two-dimensional sphere). The coordinate θ is related to the classical phase-space canonical coordinate k as $\theta = \arccos(-k/J)$, and ϕ is the conjugate angle to k [36]. Therefore, a different coherent state can be defined for each point of the phase space. The action of $U(\theta,\phi)$ on the extremal state $|J,k=-J\rangle$ produces a new state centered at the point (θ,ϕ) of the sphere, which retains the minimum uncertainty of the reference state. Systems for which the dynamical group is SU(2) are, for example, rigid rotating asymmetric molecules and spin systems.

The result of applying the unitary operator $U(\theta,\phi)$ to the reference state $|J,k=-J\rangle$ can be expressed in terms of the basis set $|J,k\rangle$ [36]

$$|\theta,\phi\rangle = \sum_{k=-J}^{k=J} \binom{2J}{J+k}^{1/2} \sin^{J+k}(\theta/2)$$
$$\times \cos^{J-k}(\theta/2)e^{-i(J+k)\phi}|J,k\rangle. \qquad (2.3)$$

These states can be expanded in terms of the eigenfunctions of H_0 for given J:

$$|\theta,\phi\rangle = \sum_{n=0}^{2J+1} c_n|J,K_a,K_c\rangle, \qquad (2.4)$$

with c_n given by

$$c_n = \langle J, K_a, K_c | \theta, \phi \rangle$$
$$= \sum_{k=-J}^{k=J} d_k^n \times \binom{2J}{J+k}^{1/2} \sin^{J+k}(\theta/2) \cos^{J-k}(\theta/2)$$
$$\times e^{-i(J+k)\phi}, \tag{2.5}$$

where d_k^n is the coefficient of the expansion of the eigenvector $|J, K_a, K_c\rangle$ in the set of symmetric-top basis functions, corresponding to $|J, k\rangle$.

A special property of AMCS's is that they are minimum uncertainty states with respect to the relations [37]

$$(\Delta J_z)^2 (\Delta \sin \phi)^2 \geq \tfrac{1}{4} \langle \cos \phi \rangle^2, \tag{2.6}$$

$$(\Delta J_z)^2 (\Delta \cos \phi)^2 \geq \tfrac{1}{4} \langle \sin \phi \rangle^2. \tag{2.7}$$

The usual uncertainty relation for J_z and its conjugate angle ϕ ($\Delta J_z \Delta \phi \geq \tfrac{1}{2}$) does not hold, since ϕ is not Hermitian with respect to $J_z | JkM \rangle$ due to the nonperiodicity of $\phi | JkM \rangle$ [38]. Nonetheless, the uncertainty relations given above reduce to the usual $\Delta J_z \Delta \phi \geq \tfrac{1}{2}$ when the wave function is strongly localized in ϕ. Another interesting property of AMCS's is that they minimize the fluctuations of the direction of the angular-momentum vector. On the other hand, AMCS's spread after some time, since the energy levels for the rigid rotor are not equally spaced, although they can show recurrences.

AMCS's were used by Martens [36] to investigate classical-quantum correspondence in a model of Coriolis coupling in polyatomic molecules, since coherent states allow the calculation of quantum surfaces of section (QSS) which can be easily compared to Poincaré surfaces of section obtained by running classical trajectories. In Ref. [39], AMCS's were used to construct QSS for a molecule containing an internal rotor to relate classical chaos with anomalous asymmetry splittings between pairs of quantum eigenvalues.

Other rotational coherent states have been studied in the past. Gulshani [8] found oscillatorlike coherent states for an asymmetric top by using the Schwinger realization of the angular-momentum algebra. He uses a transformation from the Euler angles to the so-called Cailey-Klein variables. He also discussed the relation between these wave packets and those defined by other authors. In particular, he showed that various definitions of the coherent states of the angular momentum are special cases of the generalized coherent states of the SU(2) algebra obtained by Mikhailov [40].

Since coherent states are the most classical quantum states, they are good approximations for the wave functions of the rotational Hamiltonian in the high-J limit. Huber, Heller, and Harter [41] developed a semiclassical method to calculate eigenvalues and eigenfunctions for highly excited states of asymmetric tops based on the propagation of a coherent state using Hamilton's equations.

III. MICROWAVE FIELD DESIGN

Assuming an ensemble of molecules in a pure state which can, for simplicity, be the ground state $0_{0,0}$ and a target at time t_f consisting of a generalized angular-momentum coherent state $|\theta, \phi\rangle$, the problem studied in the present paper is to determine the optimum time evolution operator $U(t_f, t_0)$:

$$\phi(t_f) \equiv |\theta, \phi\rangle = U(t_f, t_0)|J=0, K_a=0, K_c=0\rangle. \tag{3.1}$$

$U(t_f, t_0)$ can be written as

$$U(t_f, t_0) = \exp\left[\int_{t_0}^{t_f} [-i(H_0 + H'(\tau))] d\tau \right], \tag{3.2}$$

with H_0 being the molecular Hamiltonian given by Eq. (1), and $H'(\tau)$ representing the interaction at time τ between the molecular dipole moment $\boldsymbol{\mu}$ and the external electric field $\boldsymbol{\epsilon}$ directed along the laboratory-fixed Z axis [42]:

$$H'(\tau) = -\mu_Z \epsilon = (\mu_{Zx}\lambda_{Zx} + \mu_{Zy}\lambda_{Zy} + \mu_{Zz}\lambda_{Zz})\epsilon(\tau), \tag{3.3}$$

where $\mu_{Z\alpha}$ is the component of the dipole moment along the body-fixed α axis, and $\lambda_{Z,\alpha}$ is the direction cosine between the body-fixed α axis and the space-fixed Z axis.

$H'(\tau)$ can be written in a more convenient form to simplify the calculation of matrix elements [43]:

$$H'(\tau) = [\mu_{Zz}\lambda_{Zz} + (\mu_{Zx} + i\mu_{Zy})(\lambda_{Zx} - i\lambda_{Zy}) + (\mu_{Zx} - i\mu_{Zy})$$
$$\times (\lambda_{Zx} + i\lambda_{Zy})]\epsilon(\tau). \tag{3.4}$$

Direction cosine matrix elements in a basis set of symmetric-top wave functions can be found in Ref. [44]. λ_{Zz} is responsible for couplings between symmetric-top wave functions with the same k, while the terms $\lambda_{Zx} \pm i\lambda_{Zy}$ couple basis functions with $\Delta k = \pm 1$. For a given matrix elements only one of the three terms can be nonzero. Also, only matrix elements between states with $\Delta J = 0, \pm 1$ are nonzero. On the other hand, depending on the polarization characteristics of the incident light, transitions with only $\Delta M = 0$ (linear polarization) or $\Delta M = \pm 1$ (circular polarization) can be selected.

A pure state can be created, in principle, in a strong supersonic expansion for molecules with convenient values of the rotational constants, but normally a mixed state will result with a thermal distribution of rotational states. According to Hudson et al. [24], for diatomic molecules with rotational constants smaller than about 20 GHz, it is not possible to create a pure state by cooling in a strong expansion. Methods based on the density-matrix formalism have been developed to determine optimal fields to achieve specific targets when the initial state is a mixture. However it has been shown [45] that in this case a maximum limit for the achievement is imposed by the largest coefficient in the density-matrix expansion, in such a way that only a limited number of molecules from the ensemble can be placed in the target state. Girardeau et al. [45] showed that for an N-level system in which the statistical weight of all members of the ensemble is equal to $1/N$, enhancement of populations is not possible since they will remain in any case equal to $1/N$. Therefore, if we start with an ensemble described by the density matrix $\rho = \Sigma_M 1/(2J+1)|J, K_a, K_c, M\rangle\langle J, K_a, K_c, M|$ with all the M sublevels equally populated, total control is not possible since only $N/(2J+1)$ molecules could be put into the coherent state $|\theta, \phi\rangle$. In the following it is assumed that an initial ensemble described by a pure state is available.

The shape of the optimum field which guides the molecule from an initial state $|E_0\rangle$ at time t_0 to $|\theta, \phi\rangle$ at time t_f can be determined by using optimal control theory combined with Krotov's method. This method provides a local iterative scheme (see Ref. [30] for a critical comparison of local

methods and gradient or conjugate gradient methods). In the present paper the following algorithm summarized in Ref. [31] has been used.

(i) Propagate the target (in our case, the coherent state $|\theta,\phi\rangle = \psi$) backward from the target time, t_f, to t_0 using the field from the previous iteration.

(ii) Calculate the field for the new iteration $(n+1)$ at time t_0,

$$\epsilon^{(n+1)}(0) = \epsilon^{(n)}(0) - \text{Im}\langle \psi^n(0)|\mu|E_0(0)\rangle/\lambda, \quad (3.5)$$

where λ is a penalty on the energy of the field.

(iii) Use $\epsilon^{(n+1)}(0)$ to propagate $|E_0\rangle$ to time Δt.

(iv) Calculate $\epsilon^{(n+1)}(\Delta t)$,

$$\epsilon^{(n+1)}(\Delta t) = \epsilon^{(n)}(\Delta t) - \text{Im}\langle \psi^n(\Delta t)|\mu|E_0^{(n+1)}(\Delta t)\rangle/\lambda.$$
$$(3.6)$$

(v) Repeat (iii) and (iv) until $t=t_f$.

The time propagation of the initial and target wave functions is carried out by using the Riemann product integral method [46]. In this method, the unitary evolution operator is calculated as

$$U(t_f,t_0) = T\prod_{k=1}^{n} \exp\left(\int_{t_{k-1}}^{t_k} -i[H_0 - \mu\epsilon(t)]dt \right), \quad (3.7)$$

where T is the time ordering operator which arranges the product in chronological order. In other words, the interval $[t_0,t_f]$ is discretized in a number of subintervals Δt such that $H(t)$ is approximately constant in each; then the exponential matrix is evaluated for each subinterval.

A linearly polarized field has been assumed in the following calculations. Therefore, molecules in the state $|J=0,K_a=0,K_c=0,M=0\rangle$ only can reach states with $M=0$. Figure 1 shows an energy-level diagram for several J values corresponding to a hypothetical molecule with rotational constants $A=6$ GHz, $B=3$ GHz, and $C=2$ GHz, and two dipole moment components $\mu_a=1.5$ D and $\mu_b=1.2$ D, each of which gives rise to different couplings. μ_a couples levels with ΔK_a even and ΔK_c odd, while the levels coupled by μ_b have ΔK_a odd and ΔK_c odd.

The time dependence of the optimum fields to take this hypothetical molecule from the lowest eigenstate with $M=1$ ($|J=1,K_a=0,K_c=1\rangle$) to the simplest coherent state with $J=3$ ($|J=3,k=-3\rangle$), for different target times, is shown in Fig. 2. The absolute value of the Fourier transforms of the fields are also shown in this figure. The maximum field intensity increases for shorter target times. The initial field is given for a superposition of three cosine-type monochromatic fields with frequencies corresponding to the transitions $1_{1,0}\leftarrow 1_{0,1}$ (4.0 GHz), $2_{2,1}\leftarrow 1_{1,0}$ (20.0 GHz), and $3_{3,0}\leftarrow 2_{2,1}$ (32.6 GHz) (see Fig. 1). An appropriate sequence of three pulses with these three frequencies would take a molecule from $1_{0,1}$ to $3_{3,0}$. Since there are two dipole components, different routes of sequential excitation can be followed to reach the target state. For example, an initial field containing a frequency resonant with any of the energy intervals $1_{1,0}-1_{1,1}$, $2_{2,0}-2_{2,1}$, $3_{3,0}-3_{3,1}$, or containing two or even three resonant frequencies, could have been chosen, forcing in some way a preferred route. However none of these couplings were present in the initial Hamiltonian, leav-
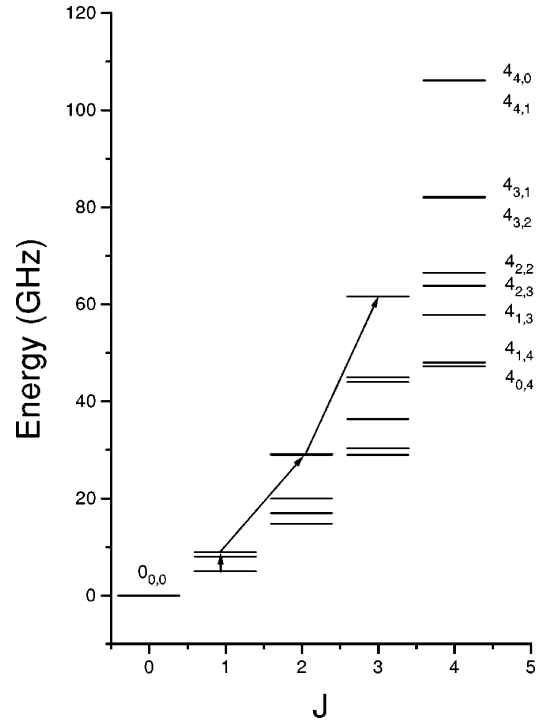

FIG. 1. Energy levels (in GHz) for the hypothetical molecule studied in this paper for several J values. The ground state and the energy levels corresponding to $J=4$ are labeled using J_{K_a,K_c} (see text). For a given J, the lowest-energy level is $J_{0,J}$ and the highest is $J_{J,0}$. For $J=2$, 3, and 4, K splittings corresponding to the highest-energy levels ($J_{J,0},J_{J,1}$) are not observable at the plot resolution. The arrows correspond to the frequencies contained in the initial electric field used to create the simplest coherent state $|J=3,k=-3\rangle$.

ing to the iterative procedure the choice of a route. The spectrum given in Fig. 2(d) shows that the algorithm has not chosen the route consisting in populating first $|J=3,K_a=3,K_c=0\rangle$ which would be possible with the field initially chosen, and then redistributing the population between $|J=3,K_a=3,K_c=1\rangle$ and $|J=3,K_a=3,K_c=0\rangle$ (these two states almost exhaust the simplest coherent state for $J=3$). However, the frequency corresponding to $2_{2,0}-1_{1,1}$ (21.2 GHz) appears in the spectrum. This frequency would not be necessary using the route just described. In other words, the procedure gives a field which takes advantage of all possible routes to populate the eigenstates that form the coherent state instead of choosing the simplest one. For longer times [Fig. 2(b)], this behavior is more evident because the line at approximately 25 GHz ($3_{3,1}-2_{1,2}$) becomes more intense than the corresponding to $2_{2,1}-1_{1,0}$. Also, a pair of closed lines centered at approximately 35 GHz can be seen in Figs. 2(b) and 2(d) [in Fig. 2(f) only a wide line is observable]. These two lines correspond to the transitions $4_{3,1}\leftarrow 4_{0,4}$ and $4_{3,1}\leftarrow 4_{1,4}$, and the field must contain them to avoid population flow to higher states.

For a molecule with only one dipole moment component, more complex routes have to be followed to reach the target. For a case in which $\mu_a\neq 0$ and $\mu_b=0$ it is not possible to populate $3_{3,0}$ starting from $0_{0,0}$ with one-photon transitions. Therefore, the target can only be reached with stronger fields.

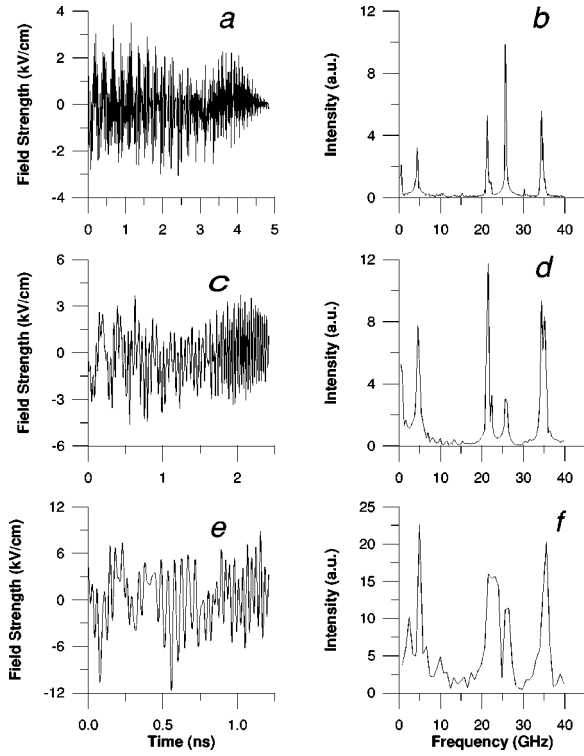Figure 3 is equivalent to Fig. 2, but the target is now the

FIG. 2. Optimum electric fields [(a), (c), and (e)] and their Fourier transforms [(b), (d), and (f)] for different target times, to guide the hypothetical molecule studied in this paper from the state $|J=1,K_a=0,K_c=1,M=1\rangle$ to the simplest coherent state $|J=3, k=-3\rangle$. Target times are (a) $t_f=4.8$ ns, (c) $t_f=2.4$ ns, and (e) $t_f=1.2$ ns.
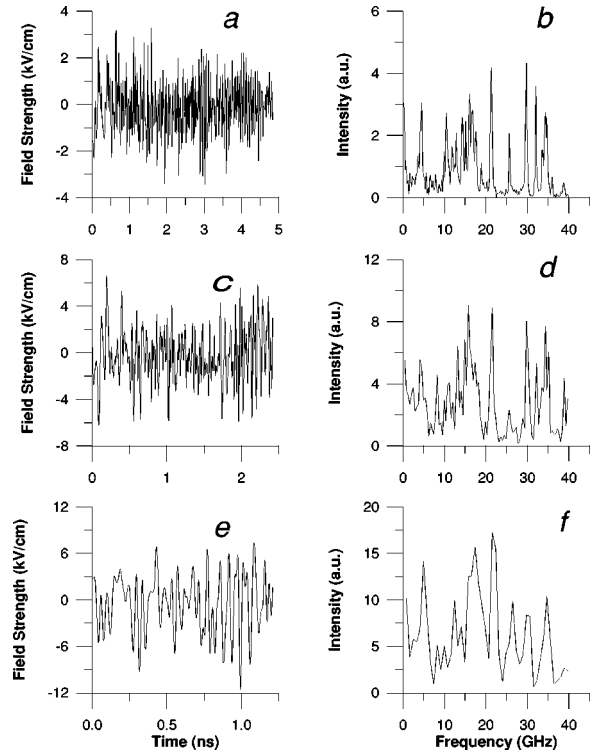
FIG. 3. Optimum electric fields [(a), (c), and (e)] and their Fourier transforms [(b), (d), and (f)] for different target times, to guide the hypothetical molecule studied in this paper from the state $|J=1,K_a=0,K_c=1,M=1\rangle$ to the coherent state $|J=3,\theta=0.7, \phi=0.1\rangle$. Target times are (a) $t_f=4.8$ ns, (c) $t_f=2.4$ ns, and (e) $t_f=1.2$ ns.

coherent state $|J=3;\theta=0.7,\phi=0.1\rangle$. The initial state is again $|J=1,K_a=0,K_c=1,M=1\rangle$. The frequency spectra for the optimum fields are more complex than those obtained when the target was the simplest coherent state, since more energy eigenstates contribute to this state. In fact, this coherent state is a combination of the seven eigenstates corresponding to $J=3$, and therefore it can be classified among the most complex coherent states, in contrast to the simplest coherent state discussed above.

IV. SUPPRESSION OF DEPHASING FOR THE SIMPLEST COHERENT STATE

As we saw in Sec. II, AMCS's are linear combinations of eigenstates of the molecule, and consequently they are nonstationary states. The free time evolution of these states after the pulse is over gives rise to dephasing among the different components of the wave packet. As a result of dephasing, the minimum uncertainty property and strong localization of the AMCS are lost, although revivals will periodically appear.

Next we will concentrate on the simplest type of angular-momentum coherent state, namely, the so-called extremal state, given by the symmetric-top wave function $|J,k=-J\rangle$. This state is mainly formed of the eigenstates $|J,K_a=J, K_c=0\rangle$ and $|J,K_a=J,K_c=1\rangle$ with small contributions from $|J,K_a=J-2,K_c=2\rangle$ and $|J,K_a=J-2,K_c=3\rangle$. In this case, the dephasing gives rise to quantum dynamical tunneling (i.e., tunneling not associated with a potential barrier), and the wave packet oscillates between the states $|J,k=-J\rangle$ and $|J,k=J\rangle$ [47].

Control of processes induced by dephasing is raising an increasing interest. Recently [19], it was shown that coherent destruction of tunneling for a particle in a symmetric double-well potential can be achieved by using a monochromatic driving force. This driving force is tuned to a suitably chosen frequency in the vicinity of an exact crossing of the two Floquet states corresponding to a doublet of close-lying states of the molecular Hamiltonian. On the other hand, Holthaus [20] showed the opposite phenomenon, i.e., the enhancement of tunneling, by using appropriately shaped smooth laser pulses. Holthaus showed that when the quasienergy difference between the pair of Floquet eigenstates involved in the tunneling doublet becomes larger than the bare tunnel splitting, the tunneling time can be much shorter than in the case of the undriven system. In the same line, Guérin and Jauslin [21] demonstrated, using Floquet theory, a different mechanism of tunneling enhancement which requires less intense laser pulses.

Another issue related to the control of dephasing is the possibility of achieving selective elimination of intramolecular vibrational redistribution (IVR) using strong resonant laser fields [48]. In this case the dephasing that causes IVR is eliminated by coherently coupling the ground state and a doorway state. The mechanism at work in this case is different from the one responsible for suppression of tunneling in the double well. Here, when the Rabi frequency is larger than the energy spread of the eigenstates involved in IVR, the doorway state becomes effectively an eigenstate of the molecule-field Hamiltonian suppressing energy-transfer processes. The limitation of this technique is obvious when the

bright state contains a large number of molecular eigenstates with a huge frequency spread.

A. Static fields

Dephasing can be suppressed for the simplest AMCS by using a static field of appropriate intensity. This is an example of Stark effect for two nearby levels, as explained in the classic book by Townes and Schawlow [44]. However, from the experimental viewpoint it would be more convenient to create coherent states with the static field on, since the time to raise the field from zero to the needed value is necessarily finite. Therefore the microwave pulses should be optimized by using the Stark eigenstates instead of the field-free molecular eigenstates.

For appropriate energy differences and dipole moment matrix elements, the coherent state becomes an eigenstate of the molecule-field Hamiltonian, and therefore the molecule will not tunnel from $+K$ to $-K$, or vice versa. However, it is not possible for every molecule to attain an exact matching with the extremal state at reasonable fields. In some cases, it is not possible for any reasonable field strength to make the extremal state an eigenstate of the molecule-field Hamiltonian, because other states begin to be significantly coupled to it. However, similar states, such that the tunneling time increases considerably for them with respect to the bare tunneling time, can be found. The extremal state $|J=3, k=-3\rangle$ for the model molecule becomes an eigenstate of the molecule-field Hamiltonian for a field of $\epsilon \approx 6$ kV/cm for the case $M=1$. Stronger fields couple the extremal state to higher states. Smaller fields ($\epsilon \approx 280$ V/cm) give rise to states similar enough to the extremal state such that no significant dephasing arises after 25 ns. In the absence of the external field the time for complete tunneling from $k=-3$ to 3 is about 15 ns. These calculations are only a rough approximation of the dynamics of a real molecule, as for these long times centrifugal distortion terms have to be taken into account in the molecular Hamiltonian. Centrifugal distortion parameters are routine in high-resolution spectroscopic analysis, and their inclusion in the kind of calculations done in the present work does not add any extra complication, since the most important centrifugal distortion factors make only diagonal contributions to the Hamiltonian.

The fact that some eigenfunctions of the molecule-field Hamiltonian are similar to extremal states does not imply that coherent states can be obtained simply by switching on an appropriate electric field suddenly, since the wave function at zero time is a molecular eigenfunction. This wave function can be expressed as a linear combination of eigenstates of the molecule-field Hamiltonian:

$$\phi(t=0) = \sum_{J,n} c_{Jn} |J, E_n\rangle_f. \tag{4.1}$$

This function evolves in time under the action of the static field as

$$\phi(t) = \sum_{J,n} c_{Jn} \exp^{-iE_{Jn}t} |J, E_n\rangle_f, \tag{4.2}$$

and consequently an uncontrolled sudden application of the field does not transform the molecular eigenfunction in the extremal state even when this is an eigenstate of the
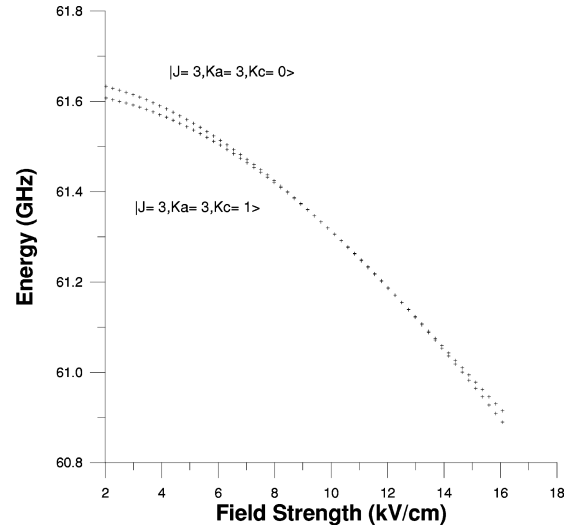

FIG. 4. Energies corresponding to the states $|J=3, K_a=3, K_c=1, M=0\rangle$ and $|J=3, K_a=3, K_c=0, M=0\rangle$ of the hypothetical molecule studied in this paper in the presence of a static electric field as a function of the field strength. These two states are nearly degenerate for a range of strengths around $|\epsilon|=10$ kV/cm.

molecule-field Hamiltonian. Under realistic conditions, collisions among molecules will eventually destroy the coherence characteristic of $\phi(t)$, placing the molecule in the extremal state. Adiabatic switching of the perturbation could also be able to guide the molecule from the initial eigenstate to the extremal state.

For $M=0$ the states $|J=3, K_a=3, K_c=0\rangle$ and $|J=3, K_a=3, K_c=1\rangle$ are not connected by the field, and therefore the extremal state cannot be an eigenstate of the molecule-field Hamiltonian. However a different mechanism can avoid the dephasing in this case. For fields about $\epsilon=10$ kV/cm, the states forming the coherent state for $J=3$ receive a small contribution from states belonging to $J=4$, which gives rise to nearly degenerate energies, as can be seen in Fig. 4. As a consequence, the extremal state will not dephase as long as the field is on.

B. Periodic fields

Periodic fields can be used to avoid dephasing, and this is especially interesting for the case with $M=0$ for which strong static fields are needed. The Schrödinger equation for an asymmetric top molecule in the presence of an external periodic field with frequency ω has quasiperiodic solutions that can be expanded as

$$\Phi(t) = e^{-i\lambda t} \sum_{n=-\infty}^{\infty} \sum_{J=0}^{\infty} \sum_{K_a, K_c} c_{(J,K_a,K_c,n)} e^{in\omega t} |J, K_a, K_c\rangle, \tag{4.3}$$

where $|J, K_a, K_c\rangle$ are the eigenstates of the molecular Hamiltonian, and λ are the quasienergies. These states are true stationary states (dressed states) of the time-dependent periodic Hamiltonian, and they can be obtained by diagonalizing a truncated representation of the infinite Floquet matrix [18].

Figure 5 shows a plot of the quasienergies as a function of the amplitude of the external field for fixed frequency. Figure 5(a) corresponds to $M=0$, and Fig. 5(b) corresponds to $M=1$. Avoided crossings between the dressed states correlated
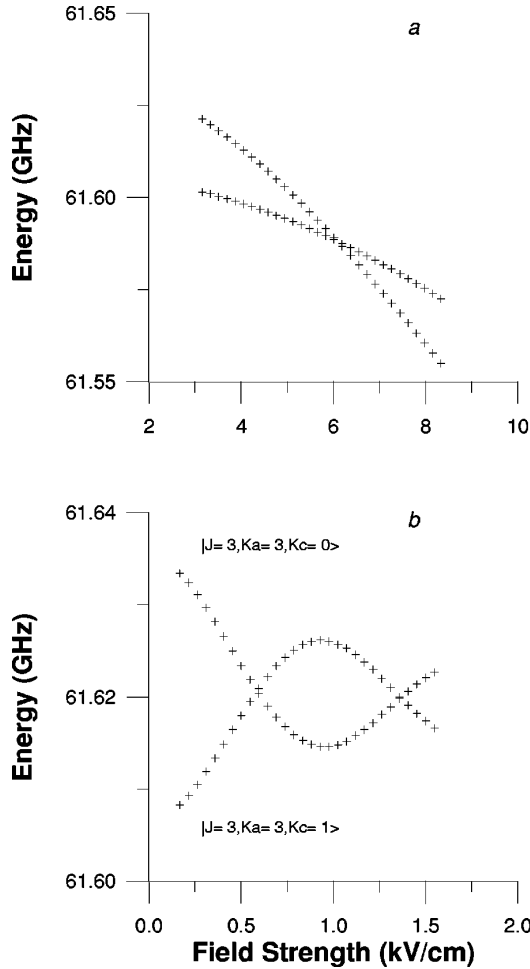
FIG. 5. Quasienergies corresponding to the states correlated adiabatically with the zero-field states $|J=3,K_a=3,K_c=1\rangle$, $|J=3,K_a=3,K_c=0\rangle$ of the hypothetical molecule studied in this paper in the presence of an oscillating electric field as a function of the field strength. (a) corresponds to $M=0$ and $\omega=1.5$ GHz, and (b) to $M=1$ and $\omega=93$ MHz.

adiabatically with the two eigenstates forming the coherent state take place at different field intensities for different frequency values. At the crossing point the two dressed states have components belonging to several photon states. For example, for the case $M=0$ there is an avoided crossing at $\epsilon=6.1$ kV/cm and $\omega=1.5$ GHz. For $M\neq0$, due to the different dipole couplings, the dressed states involve more photon states. For example, the extremal state with $M=1$ evolves in time according to

$$\phi(t)\simeq0.7|J=3,K_a=3,K_c=0\rangle\left(\sum_n c_n|e^{in\omega t}\rangle\right)e^{-i\lambda_{3,3,0}t}$$

$$+0.7|J=3,K_a=3,K_c=1\rangle\left(\sum_n c_n|e^{in\omega t}\rangle\right)e^{-i\lambda_{3,3,1}t},$$

where $\lambda_{3,3,0}$ and $\lambda_{3,3,1}$ are the quasienergies of the dressed states correlated to the zero-field states $|J=3,K_a=3,K_c=0\rangle$ and $|J=3,K_a=3,K_c=1\rangle$. For the avoided crossing corresponding to $\epsilon=0.59$ kV/cm and $\omega=93$ MHz, the coefficients entering into both summations are nearly the same. Therefore the wave function can be simplified to

$$\phi(t)\simeq0.7(|J=3,K_a=3,K_c=0\rangle+|J=3,K_a=3,K_c=1\rangle)$$

$$\times\sum_n c_n|e^{in\omega t}\rangle e^{-i\lambda t}\simeq|J=3,K=3\rangle e^{-i\delta t}.$$

The time evolution of this wave function is therefore trivial under the action of the appropriate field, and the state will remain coherent forever in the absence of spontaneous emission or collisions.

V. CONCLUSIONS

It has been shown here that angular momentum coherent states could be experimentally obtained for a semirigid asymmetric top molecule by using tailored microwave pulses. Some requirements on the rotational constants (since power and bandwith are anticorrelated [24]) and dipole moment are needed to achieve this goal with feasible pulses. An AMCS comprises, in principle, the $2J+1$ rotational eigenstates corresponding to a particular J, and therefore, the required bandwidth to create a rotational coherent state for a near prolate asymmetric top will be, approximately, $2AJ+B$.

For molecules with two nonzero dipole moment components, couplings to connect all the rotational levels are available, and therefore it is easier to create AMCS's than for molecules with only one nonzero component, for which stronger fields are needed. On the other hand, due to the complex energy-level structure of asymmetric-top molecules, small dipole moments can be enough to create AMCS's. For the dipole components of the model molecule chosen in this paper ($\mu_a=1.5$ D and $\mu_b=1.2$ D), AMCS's can be created with fields around 5 kV/cm. The method is quite general, and AMCS's could be produced in numerous molecules.

Due to the fact that the simplest coherent state $|J,k=-J\rangle$ consists mainly of the two components of a cluster doublet (angular momentum analog of inversion doublet levels of a two-well oscillator potential [47]), dephasing gives rise to dynamical tunneling that can be suppressed by the application of external fields.

Interesting dynamical aspects could be analyzed from the study of AMCS's. For example, it was shown in Ref. [39] that some rotational eigenstates of torsional states of acetaldehyde have anomalously large asymmetry splittings. This was explained in Ref. [39] as chaos-enhanced quantum-mechanical tunneling. When the maxima of the Husimi representation of the involved eigenvectors lie in chaotic regions of the phase space, the dynamical tunneling is enhanced and the asymmetry splittings increase. An experiment could be devised in which rotational coherent states for a torsional eigenstate close to the barrier to internal rotation were created. Then the behavior of AMCS's lying in chaotic regions of the classical phase space could be compared to the behavior of AMCS's lying in regular regions, looking for distinctive characteristics.

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