

Pendular States of Highly Vibrationally Excited Molecules

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The behavior of coherent field-induced hybrids of field-free rotor states ("pendular states") is studied in energy regions where intramolecular vibrational energy redistribution phenomena are important. The energy region corresponding to the $4\nu_1$ band system of HCCF molecules, at approximately $12\,800\text{ cm}^{-1}$, has been chosen as an example. The calculations show that the expectation value of the orientation of molecules prepared in nonstationary pendular bright states exhibits a slow decay to the equilibrium value. Therefore the molecules substantially conserve their initial orientation after intramolecular vibrational redistribution takes place. [S0031-9007(99)08810-9]

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Over the past decade, a large effort has been devoted to developing methods to align or orient molecules to study steric effects in collisions between molecules or between molecules and surfaces [1]. Various techniques have been developed for creating distributions of molecules which are aligned or oriented with respect to a space-fixed axis, including using inhomogeneous electric fields to focus molecules in specific $J, |M|$ levels [2] (J is the rotational angular momentum quantum number and M the corresponding projection along a space-fixed axis), polarized lasers to preferentially excite high or low $|M|$ levels [3], supersonic-nozzle expansions to align and orient molecules via velocity slippage in the expansion [4], or large static electric fields to orient molecules via the high-field Stark effect [5,6].

Often these techniques are used in combination with lasers to create vibrationally or electronically excited molecules which are aligned or oriented. When pulsed lasers are used, new difficulties arise due to the possibility of exciting a nonstationary state of the molecular Hamiltonian. The time-dependent behavior of the state can lead to the degree of orientation or alignment changing during the time scale of the experiment. Orr-Ewing *et al.* [3] have explored this problem in the case of using a linearly polarized pulsed laser to create an aligned state for $v = 1$ HCl. Since the excitation bandwidth overlaps the hyperfine splitting pattern of the spin 3/2 quadrupolar nucleus of the Cl, the excited-state alignment oscillates in time at a rate dependent on the magnitude of the coupling of the rotational angular momentum with the nuclear spin.

Alternatively, the large electric-field methods of Friedrich and Herschbach [5] and Loesch and Remscheid [6] can be employed. Their techniques use a large electric field to "brute-force" orient the molecular dipole moment about the field axis, by creating bound states ("pendular states") within the Stark potential. As pointed out by Friedrich and Herschbach, one advantage of this technique when hyperfine structure is present is that the large

electric field forces the uncoupling of the nuclear spin from rotation and instead couples both angular momenta strongly to the field axis, thus reducing the problematic hyperfine effects in the orientation experiments. In this Letter we present calculations that demonstrate the feasibility of extending these techniques to highly vibrationally excited molecules, which participate in reactions in many chemically important environments.

As in the hyperfine case, for molecules excited to a region of high vibrational state density where intramolecular vibrational energy redistribution (IVR) [7] occurs, additional complications need to be considered when designing experiments which require that the excited-state molecules be aligned or oriented. Recently, it has been shown that a molecule excited to a single molecular eigenstate in regions of high state density is no longer deflected by inhomogeneous electric fields when the mean spacing between vibrational levels is on the order of the mean molecule-field interaction strength [8]. This effect originates from the multitude of avoided crossings that the eigenstates experience during the time the molecule travels through the electric-field region, preventing the required force needed for deflection from being applied to the molecule. Moreover, using incoherent high-temperature thermal excitation combined with electric deflection to attempt to achieve aligned or oriented distributions of highly vibrationally excited molecules may meet with analogous difficulties, as shown by Farley *et al.* [9].

Problems also arise when using lasers to achieve orientation of the electric dipole moment or internuclear axis in regions of high density of states, due to the complex vibrational dynamics. Nathanson and McClelland [10] have discussed these points extensively in their investigation of fluorescence polarization and IVR. They find that complex vibrational dynamics can appreciably reduce fluorescence polarization if significant vibration-rotation coupling is present. In the case of orientation experiments using polarized light, the complex vibrational dynamics have slightly

different effects depending on the excitation mechanism used to achieve the orientation. Excitation of a single molecular eigenstate component of an IVR fractionated "bright-state" transition [11] will generally give rise to an oriented state with unknown properties, unless significant effort has been undertaken to determine the progenitors of the state. On the other hand, coherent excitation of the IVR multiplet using a pulsed laser will prepare a nonstationary state of the molecular Hamiltonian whose electric dipole or axes orientation could oscillate and even decay nearly irreversibly, at a rate dependent on the strength of the coupling between rotation and vibration.

In the present Letter we present dynamical calculations, using the HCCF molecule as a model, of the time dependence of the molecule orientation in a strong static field following coherent excitation of the $\nu = 4$ CH overtone stretch vibrational transition. Here, HCCF is chosen for study since the anharmonic force field is well characterized, allowing a realistic description of the energy levels and couplings in the high-density-of-states regime.

The rovibrational energy levels (measured from the vibrational ground state) of HCCF in the presence of a strong static electric field can be obtained from a Hamiltonian expressed in rectilinear normal coordinates, Q_r , as given in Ref. [12],

$$H = \sum_r \nu_r \nu_r + x_{rr}(\nu_r^2 - \nu_r) + \sum_{r < r'} \sum_{r''} x_{rr''} \nu_r \nu_{r''} + \sum_t g_{tt}(l_t^2 - \nu_t) + \sum_{t < t'} \sum_{t''} g_{tt''} l_t l_{t''} + k_{123} Q_1 Q_2 Q_3 + k_{233} Q_2 Q_3 Q_3 + k_{344} Q_3 Q_4 Q_4 + k_{345} Q_3 Q_4 Q_5 + B_v J(J+1) - \mu_v \varepsilon \cos \theta, \quad (1)$$

where ν_r is the number of vibrational quanta in the normal mode r and l_t is the vibrational angular momentum for a degenerate bending vibration t . The k_{ijl} are cubic force constants which cause strong Fermi couplings. The contribution from the nonresonant part of the anharmonic potential is given by the Dunham-type constants $x_{rr'}$ and $g_{tt'}$; B_v and μ_v give, respectively, the vibrational dependence of the rotational constant and dipole moment; ε is the electric-field strength and θ is the instantaneous angle between the molecular axis and the electric-field direction. Numerical values for the constants contained in H were taken from Table III of Ref. [12]. Coriolis coupling or centrifugal distortion effects, which are not very significant for low J , as supported by the rotational analysis of overtone spectra in Refs. [12,13], have not been considered in our model. Our dipole-moment function, μ_v , is a Padé approximant [14] obtained from a fit of the Stark measurements reported in [15] for several vibrational states. The small value of the equilibrium dipole moment (0.7 D) makes necessary the use of unrealistic electric fields to create pendular states; however, the same effects should be attainable with smaller electric fields for other molecules with a higher μ/B ratio [5].

The Hamiltonian matrix can be divided into polyad matrices as explained in Ref. [12]. The eigenstates of the polyad matrix corresponding to the $4\nu_1$ band system were obtained using a two-step procedure. In the first step the field-free pure vibrational problem is solved using a basis set selection based on the so-called artificial intelligence methods developed by Marcus and co-workers [16,17]. These methods are based on tier schemes; starting from a particular set of zeroth-order states a search of the most important paths connecting these to other zeroth-order states is performed. Dynamical properties, such as the IVR lifetime of a nonstationary state, can be obtained with high accuracy because they depend only on the states strongly coupled to an initial bright state [17]. An incomplete path

search using evaluation function EF_3 of Lederman and Marcus [16] was done, reducing the number of vibrational basis functions from 2781 to 825. In this model, the $4\nu_1$ ($J = 0$) transition is fractionated into twelve main components which span a spectral window of approximately 46 cm^{-1} . In the second step the complete Hamiltonian is set up in the basis set formed by the direct product of 83 anharmonic states obtained in the first step (those with a nonzero contribution from the bright state $|\nu_{\text{CH}} = 4\rangle$), and 12 rigid-rotor wave functions with $M = 0$, which, for the electric fields used, gives converged results.

Our interest is the study of the time evolution of pendular states of the vibrational bright state $|\nu_{\text{CH}} = 4\rangle$. For this purpose, a better insight can be achieved by expanding the eigenstates in the basis set formed by the direct product of zero-order vibrational states $|\nu_i\rangle$, and pendular states $|\tilde{J}, M\rangle^{\nu_i}$, with \tilde{J} the J value of the field-free progenitor $|\nu_i; J, M\rangle$ which adiabatically correlates with the high-field state. The vibrational dependence of both the rotational constant and the dipole moment gives rise to pendular states which are not, in general, orthogonal for different vibrational states. Therefore, pure anharmonic terms in the Hamiltonian connect pendular states with different \tilde{J} and ν_i . The magnitude of these couplings depends on the distribution of dipole moments and rotational constants within the vibrational bath states, and on the strength of the electric field.

Suppose that a pure pendular state of the vibrational bright state is coherently excited [18]. Figure 1 shows, for two different electric-field strengths and two different initial pendular states with $M = 0$, the survival probability $|\langle \nu_{\text{CH}} = 4; \tilde{J}, M | \phi(t) \rangle|^2$, and the pendular survival probability $\sum_i |\langle \nu_i; \tilde{J}, M | \phi(t) \rangle|^2$ (the index i runs over the zero-order vibrational states), with $\phi(t)$ being the propagated pendular bright state at time t . As expected for a small molecule with strong resonances [19] the IVR lifetime is very short (approximately 700 fs) and does not show

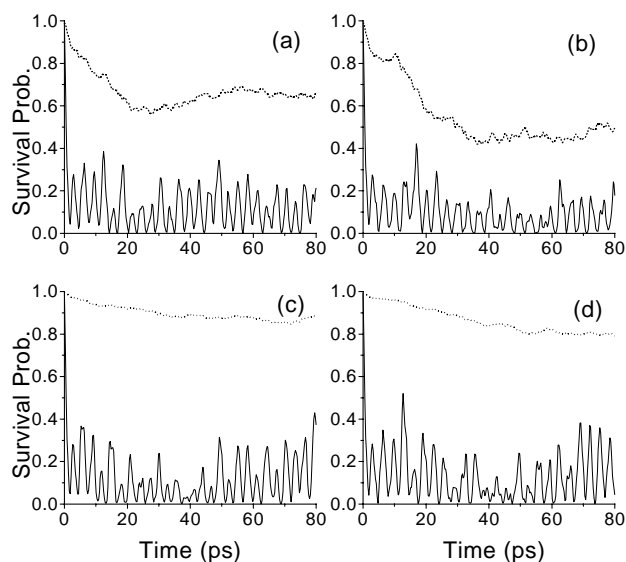


FIG. 1. Survival probability (solid lines) for different pendular bright states with $M = 0$, and pendular survival probability (dotted lines). Electric fields and initial wave functions are (a) $\varepsilon = 600$ kV/cm, $|v_{CH} = 4; \tilde{J} = 1\rangle$, (b) $\varepsilon = 300$ kV/cm, $|v_{CH} = 4; \tilde{J} = 1\rangle$, (c) $\varepsilon = 600$ kV/cm, $|v_{CH} = 4; \tilde{J} = 0\rangle$, and (d) $\varepsilon = 300$ kV/cm, $|v_{CH} = 4; \tilde{J} = 0\rangle$.

any significant dependence on the electric-field strength or the rotational composition of the excited state. The pendular survival probabilities show the decay of the initial pendular state into states with different pendular character, and they exhibit relaxation to their equilibrium values [20] in a temporal scale which depends strongly on the external field and the pendular character of the initial state. Thus, the pendular state $|v_{CH} = 4; \tilde{J} = 0\rangle$, which is strongly bounded by the field, shows a slower relaxation than $|v_{CH} = 4; \tilde{J} = 1\rangle$.

Figure 2 shows the time evolution of $\langle \cos \theta \rangle$, which is a measure of orientation, for the same initial pendular bright states of Fig. 1. Molecules excited to $|v_{CH} = 4; \tilde{J} = 0\rangle$ maintain a high value of $\langle \cos \theta \rangle$ for the times shown. The short-range oscillations are due to the different values of $\langle \cos \theta \rangle$ for the pendular states with $\tilde{J} = 0$ belonging to the different normal-mode states with which the initial bright state mixes during IVR. The slow decay on orientation is due to the contamination of the wave function by pendular states with $\tilde{J} \neq 0$ (for which $\langle \cos \theta \rangle$ is smaller) which increases with time. For $\varepsilon = 600$ kV/cm the equilibrium is reached around 80 ps, and therefore after this time the average orientation does not show further decay. For the initial state $|v_{CH} = 4; \tilde{J} = 1\rangle$, at the electric fields shown in Fig. 2, the orientation undergoes much stronger short-range oscillations because the distribution of $\langle \cos \theta \rangle$ over the normal-mode vibrational states is wider for pendular states labeled $\tilde{J} = 1$ than for those with $\tilde{J} = 0$. Also the long-range decay is more important due to the larger overlap integrals for pendular states with $\tilde{J} = 1$.

These results are also relevant to state focusing. Fraser and Pate [8] showed that nondeflection behavior in en-

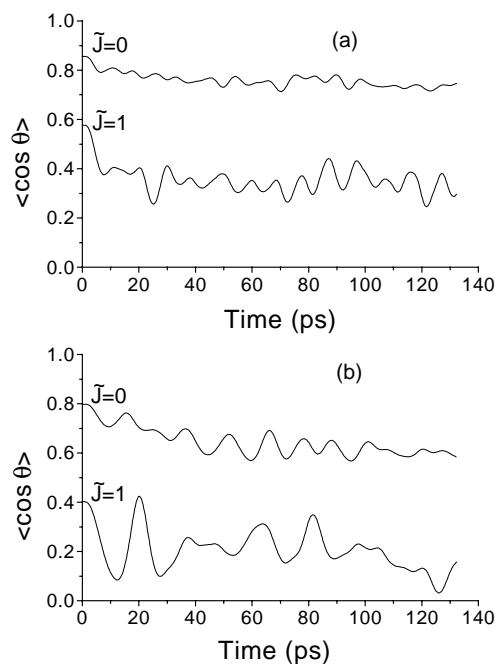


FIG. 2. Expectation value of $\cos \theta$ as a function of time for two different static fields (a) $\varepsilon = 600$ kV/cm, and (b) $\varepsilon = 300$ kV/cm. In each plot the time evolution for two different initial pendular states with $M = 0$ (as labeled in the figure) of the vibrational bright state is shown.

ergy regions where IVR is prevalent arises due to the large number of avoided crossings that a molecule experiences when traveling in an inhomogeneous field. The mechanism responsible for this behavior is again the nonorthogonality of the pendular wave functions between different normal-mode states, which gives rise to couplings between pendular states belonging to different vibrational states. Our calculations support those ideas, as can be seen in Fig. 3, which shows the variation of the molecule-field rovibrational eigenvalues of HCCF as a function of the electric-field strength. Molecules will be described at any time, in the adiabatic limit, by a single molecule-field eigenstate, and consequently the curves in Fig. 3 can be understood as eigenvalue trajectories in a slow-varying time-dependent field. As the field increases, the coupling among the zero-order states is stronger, and more eigenstates will have a significant contribution from the pendular bright state. This produces an augmented number of avoided crossings and, consequently, a flattening of the trajectories. This effect is more important for higher pendular states, as shown in Fig. 3.

We conclude that IVR leads to no loss of orientation if μ/B is constant for the different states involved in the dynamics. However, with μ/B variation there is a two-time-scale process: (i) rapid equilibration to the vibrational average $\langle \cos \theta \rangle$ for the pendular state $|\tilde{J}, M\rangle$, and (ii) slower loss of orientation from mixing in of higher (less oriented) pendular states due to the nonorthogonality of the pendular wave functions between different

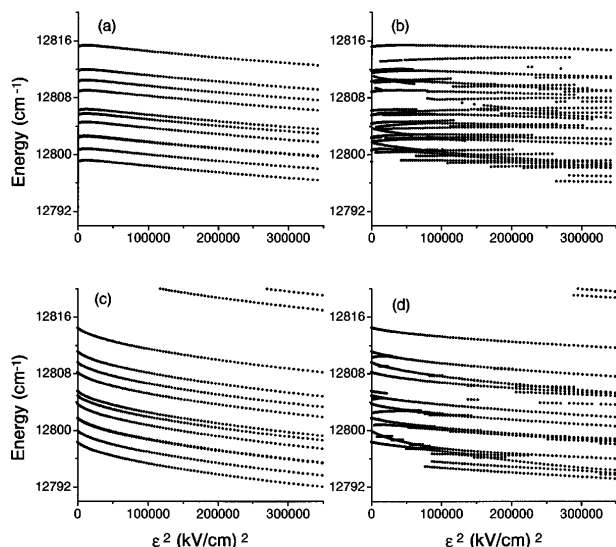


FIG. 3. Eigenvalue trajectories in a 28 cm^{-1} window of the $4\nu_1$ energy region of HCCF for energy levels with $M = 0$ versus the square of the electric field strength. Only levels with a projection along the field-dependent pendular state $|v_{\text{CH}} = 4; \tilde{J}\rangle$ larger than 0.05 are plotted, with $\tilde{J} = 1$ in (b), and $\tilde{J} = 0$ in (d). Plots labeled (a) and (c) correspond to a calculation in which the vibrational dependence of both the dipole moment and the rotational constant were turned off, showing that this dependence is responsible for the flattening of trajectories and the increase in the number of coupled states exhibited in (b) and (d).

zero-order vibrational states. On the other hand, if μ/B does not vary all states have the same Stark trajectories and, therefore, molecules in an inhomogeneous field should deflect. The μ/B variation leads to avoided crossings between states with opposite Stark shifts. These effects give rise to the types of curves observed in [8]. Therefore, the key issue in understanding how IVR affects Stark properties is the distribution of dipole moments and rotational constants (which are poorly known for highly vibrationally excited molecules) for the states involved in the quantum dynamics.

We have shown by using reasonable estimates of B and μ distributions for a well studied molecule (HCCF) that it appears possible to achieve oriented, vibrationally excited molecules in the presence of rapid IVR.

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