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Pendular trapping conditions for ultracold polar molecules enforced by external electric fields

Ming Li^a, Alexander Petrov^{a,b}, Constantinos Makrides^{a,c}, Eite Tiesinga^c and Svetlana Kotochigova^{a*}

^{*}Corresponding author. Email: skotoch@temple.edu

^a*Department of Physics, Temple University, Philadelphia, PA 19122-6082, USA*

^b*St. Petersburg Nuclear Physics Institute, Gatchina, 188300; Division*

of Quantum Mechanics, St. Petersburg State University, 198904, Russia

^c*Joint Quantum Institute and Joint Center for Quantum Information and Computer Science, National Institute of Standards and Technology and University of Maryland, Gaithersburg MD 20899, USA*

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We theoretically investigate trapping conditions for ultracold polar molecules in optical lattices, when external magnetic and electric fields are simultaneously applied. Our results are based on an accurate electronic-structure calculation of the polar $^{23}\text{Na}^{40}\text{K}$ polar molecule in its absolute ground state combined with a calculation of its rovibrational-hyperfine motion. We find that an electric field strength of 5.26(15) kV/cm and an angle of 54.7° between this field and the polarization of the optical laser lead to a trapping design for $^{23}\text{Na}^{40}\text{K}$ molecules where decoherence due to electric field strength and laser-intensity fluctuations, as well as fluctuations in the direction of its polarization, is kept to a minimum. One standard deviation systematic and statistical uncertainties are given in parenthesis. Under such conditions pairs of hyperfine-rotational states of $v = 0$ molecules, used to induce tunable dipole-dipole interactions between them, experience ultrastable, matching trapping forces.

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I. INTRODUCTION

The successful creation of near quantum-degenerate gases of polar molecules in their absolute rovibrational ground state (*e.g.* KRb [1], RbCs [2, 3], NaK [4], and NaRb [5]), opened up the possibility of studying controlled collective phenomena, ultracold chemistry, quantum computing, and of performing precision measurements with polar molecules. In most of these applications polar molecules likely need to be held in periodic, optical potentials induced by external laser fields, where two or more of their rotational hyperfine states are manipulated and accurate measurement of the transition frequency between these levels is required.

Dynamic Stark shifts of these hyperfine levels in the presence of trapping laser fields are generally different, depending on a range of experimental parameters. As a result the system is sensitive to laser-intensity fluctuations leading to uncertainties in the transition-energy measurements or decoherence when attempting to couple the states of interest for quantum control. Thus, a careful selection of trapping conditions, where a pair of internal states experience identical trapping potentials, can bring substantial benefits. Such experimental conditions are called *magic*.

Magic electric-field values for polar molecules have applications in the realm of many-body, non-equilibrium spin physics. This includes samples of molecules with long-range dipole-dipole interactions tailored by static electric fields or by a combination of electric and resonant microwave fields [6–8]. Working at a *magic* electric field, for example, ensures that spatial laser-intensity inhomogeneities across a large sample do not significantly change the resonant condition for the microwave field. Initial experimental realizations applied electric fields up to a few kV/cm. Larger electric field apparatuses are now under development [9, 10] with fields above 10 kV/cm promising larger dipole moments and individual addressing and detection.

In a previous study [11], we calculated the dynamic or AC polarizability of polar KRb and RbCs molecules. We located optical frequency windows, where light-induced decoherence is small, and determined van-der-Waals potentials between the molecules [12]. We matched the AC polarizability of the $N = 0$ and $N = 1$ rotational states of these molecules with a *magic* electric field and angle between laser polarization and electric field direction in Ref. [13]. In parallel, optimal trapping conditions for homonuclear Rb₂ and Cs₂ were studied in Refs. [14, 15].

For the KRb molecule we extended our calculations by including hyperfine coupling between molecular rotation and the nuclear electric quadrupole moment and found good agreement with experiment [16]. The coherence time for a rotational superposition was maximized at the *magic* angle. Recently, Ref. [17] suggested that the coherence time is now limited by laser-intensity fluctuations across the molecular sample. Finally, in Ref. [18] we performed an investigation for rovibronic states of $^{40}\text{K}^{87}\text{Rb}$ when three external fields are present, i.e. magnetic, electric and trapping-laser fields. The magnetic field was relatively large with a strength near 50 mT and hyperfine coupling between the nuclear spins and other angular momenta had a negligible effect.

In the current study we propose alternative means to extend coherence times for superpositions of molecular

rotational states. We focus on decreasing the dependence of the difference of their dynamic polarizabilities on electric-field and light-intensity fluctuations with respect to intensity by orienting polar molecules in a strong uniform electric field and creating so called *pendular* rotational states [19–22]. In such arrangement the DC Stark effect dominates and the complex coupling between hyperfine states with different Stark shifts simplifies.

We present a theoretical study of the dynamic polarizability of rotational hyperfine states of ultracold NaK molecules. The NaK molecule has a large permanent electric dipole moment and is chemically stable against atom-exchange reactions [23]. A long-lived quantum gas of fermionic $^{23}\text{Na}^{40}\text{K}$ molecules was created in its absolute ground state using a magnetic field of 8.57 mT [24]. Each of its rotational states $|N, m\rangle$ has 36 hyperfine states. At this magnetic field the hyperfine coupling between nuclear spins and orbital angular momenta is strong and combined fluctuations in the magnetic and electric field and trapping laser can induce drastic changes in the complex hyperfine structure. On the other hand, due to the large dipole moment of polar molecules, our static electric field will force a simplification of the hyperfine structure.

The paper is set up as follows. In Sec. II, we present the molecular Hamiltonian for ground-state alkali-metal dimers and the pendular model for strong electric fields. In Sec. III, we apply our theory to non-reactive $^{23}\text{Na}^{40}\text{K}$ to elucidate the role of an electric field, and give its *magic* trapping conditions. We summarize in Sec. IV.

II. THEORY

The effectiveness of trapping ultracold polar alkali-metal molecules with optical lasers is determined by the (real) dynamic polarizability of their ro-vibrational-hyperfine states. The polarizability of a molecular eigenstate i with energy \mathcal{E}_i under the influence of a linearly-polarized laser with frequency ω and intensity I_{trap} is defined as the derivative $\alpha_{\text{dyn},i} = -d\mathcal{E}_i/dI_{\text{trap}}$. The dynamic polarizability can then be studied as a function of the strength and orientation of static magnetic and electric fields. Eigenenergies of hyperfine states need to be calculated with care. The starting point is an effective molecular Hamiltonian that contains all *internal* and *external* interactions. It is described in subsection II A.

With even a moderate electric field, the DC Stark effect together with the rotational energy dominate over other interactions. A simplified, pendular model is then sufficient. It is given in subsection II C and will provide physical insight as well as an easy way to calculate the total polarizability in this regime.

A. Molecular Hamiltonian

We focus on rotational, hyperfine states of the lowest vibrational level of the ground singlet $X^1\Sigma^+$ electronic potential of alkali-metal dimers in the presence of a magnetic and electric field as well as a trapping laser. Our notation and conventions for angular momentum algebra are based on Ref. [25]. The effective Hamiltonian is [18, 26]

$$H = H_{\text{rot}} + H_{\text{hf}} + H_Z + H_E + H_{\text{pol}}, \quad (1)$$

where

$$H_{\text{rot}} = B_{v=0} N^2, \quad H_{\text{hf}} = \sum_{k=a,b} \mathbf{V}_k \cdot \mathbf{Q}_k, \\ H_Z = - \sum_{k=a,b} g_k \mu_B \mathbf{I}_k \cdot \mathbf{B}, \quad H_E = -\mathbf{d} \cdot \mathbf{E},$$

and

$$H_{\text{pol}} = -\frac{1}{3}[\alpha_{\parallel}(\omega) + 2\alpha_{\perp}(\omega)]I_{\text{trap}} \\ -\frac{\sqrt{6}}{3}[\alpha_{\parallel}(\omega) - \alpha_{\perp}(\omega)]T_2(\hat{\epsilon}, \hat{\epsilon}) \cdot C_2(\alpha, \beta)I_{\text{trap}}.$$

The rotational H_{rot} and hyperfine H_{hf} Hamiltonian describe the *internal* field-free molecular interactions. Here, \mathbf{N} is the rotational angular momentum operator of the molecule and $B_{v=0}$ is the rotational constant of vibrational state $v = 0$. The hyperfine Hamiltonian is the nuclear electric-quadrupole interaction, where \mathbf{Q}_k is the electric quadrupole moment of nucleus $k = a$ or b and \mathbf{V}_k is the electric field gradient generated by the electrons at the position of that nucleus. For nuclear spins \mathbf{I}_k with quantum number $I_k > 1$ this interaction is equivalent to

$$H_{\text{hf}} = \sum_{k=a,b} \frac{(eqQ)_k}{I_k(I_k - 1)} T_2(\mathbf{I}_k, \mathbf{I}_k) \cdot C_2(\alpha, \beta), \quad (2)$$

where $C_{lm}(\alpha, \beta) = \sqrt{4\pi/(2l+1)}Y_{lm}(\alpha, \beta)$ is a modified spherical harmonic, $Y_{lm}(\alpha, \beta)$ is the spherical harmonic of rank l , Euler angles α and β describe the orientation of the interatomic axis in a space-fixed coordinate frame, $T_{2m}(\mathbf{I}_k, \mathbf{I}_k)$ is the rank-2 spherical tensor constructed from nuclear spin operators and $(eqQ)_k$ is the nuclear electric-quadrupole coupling constant.

The effects of the static magnetic field, the static electric field, and the trapping laser field are included through the *external* nuclear Zeeman Hamiltonian H_Z , the DC Stark effect H_E , and molecule-laser interaction H_{pol} , respectively. In H_Z , g_k is the gyromagnetic ratio of nucleus k , \mathbf{B} is the magnetic field, and μ_B is the Bohr magneton. In H_E , the operator \mathbf{d} is the vibrationally-averaged molecular dipole moment and \mathbf{E} is the static electric field. The Hamiltonian H_{pol} depends on the frequency-dependent vibrationally-averaged parallel and perpendicular polarizabilities $\alpha_{\parallel}(\omega)$ and $\alpha_{\perp}(\omega)$, and laser intensity I_{trap} . The two rank-2 tensor operators capture

its dependence on (linear) laser polarization $\hat{\epsilon}$ and rotational state of the molecule [13]. (The $\alpha_{\parallel}(\omega)$ and $\alpha_{\perp}(\omega)$ will be further discussed in Sec. III A.) We neglect contributions from centrifugal distortions, the rotational Zeeman interaction, and other hyperfine terms.

B. Basis set, coordinate system, and quantization axis

It is convenient to find the eigenstates of Eq. 1 using the uncoupled molecular hyperfine states

$$|N, m, m_a, m_b\rangle \equiv \phi_{v=0}(r) Y_{Nm}(\alpha, \beta) |\Lambda\rangle |I_a, m_a\rangle |I_b, m_b\rangle, \quad (3)$$

where $\phi_{v=0}(r) Y_{Nm}(\alpha, \beta)$ is the $v = 0$ radial vibrational and rotational wavefunction as a function of the internuclear separation and orientation $\vec{r} = (r, \alpha, \beta)$ in spherical coordinates. The function $\phi_{v=0}(r)$ is to good approximation independent of the rotational quantum number N when N is small. The kets $|\Lambda\rangle$ and $|I_k, m_k\rangle$ describe the electronic and nuclear-spin wavefunctions, respectively.

The projection quantum numbers and angles are defined with respect to a coordinate system and quantization axis. With zero or very small electric fields, the natural quantization axis is along the magnetic-field direction \mathbf{B} . For even moderate electric fields it becomes more convenient to define the quantization axis along \mathbf{E} . In this study, we define our quantization axis along the direction of the electric field but choose our space-fixed \hat{z} axis along \mathbf{B} . Consequently, the Euler angles are defined with respect to the electric-field direction. For convenience, the laser propagates along our \hat{y} axis and its polarization $\hat{\epsilon}$ lies in the xz plane. Finally, θ is the angle between $\hat{\epsilon}$ and \mathbf{B} and ψ_m is the angle between $\hat{\epsilon}$ and \mathbf{E} .

We numerically solve for the eigenstates of Eq. 1 by including basis states from $N = 0$ up to N_{\max} . This corresponds to $(N_{\max} + 1)^2 (2I_a + 1)(2I_b + 1)$ basis states. In the absence of an electric field $N_{\max} = 1$ is sufficient. For increasing electric field, N_{\max} must be increased as coupling to higher-lying angular momentum states becomes more and more important.

C. Pendular model for large electric fields

For a finite electric field H_E quickly dominates, along with H_{rot} , over the other terms in Eq. 1. Hence, it is beneficial to investigate the energy structure of $H_0 = H_{\text{rot}} + H_E$ in the basis $|N, m\rangle \equiv \phi_{v=0}(r) Y_{Nm}(\alpha, \beta) |\Lambda\rangle$, where the quantization axis is chosen along \mathbf{E} . In our model the dipole moment \vec{d} in the DC Stark Hamiltonian has spherical components $d_q = d_{v=0} C_{1q}(\alpha, \beta)$, where $d_{v=0} = \int_0^\infty dr \phi_{v=0}(r) \mathcal{D}(r) \phi_{v=0}(r)$ is the N -independent vibrationally-averaged dipole moment and $\mathcal{D}(r)$ is the r -dependent permanent electric dipole moment of the $X^1\Sigma^+$ ground electronic state.

With our choice of quantization axis the electric field only couples basis states $|N, m\rangle$ with the same m and N that differ by one unit. In fact, for each m , H_0 is a symmetric tridiagonal matrix with non-zero matrix elements $\langle N, m | H_0 | N, m \rangle = N(N+1)B_v$ and

$$\langle N, m | H_0 | N+1, m \rangle = \frac{m^2 - (N+1)^2}{\sqrt{(2N+1)(2N+3)}} d_{v=0} E. \quad (4)$$

Its pendular eigenstates $|\lambda, m\rangle$ with $\lambda = 0, 1, \dots$ and corresponding eigenvalues $\mathcal{E}_{\lambda, m}$ have been extensively studied in the context of the molecular orientation and alignment [19–21] and are obtained through numerical diagonalization. At zero electric field strength $\lambda = N$. For increasing field strengths eigenstates of H_0 with the same λ but different $|m|$ separate away from each other, leaving a double degeneracy for states with $m \neq 0$.

The polarizability of pendular states is determined from the derivative of eigenenergies of $H_0 + H_{\text{pol}}$ with respect to the laser intensity. For optical laser photons with an energy that is orders of magnitude larger than B_v (and even vibrational spacings), the N -independent polarizabilities $\alpha_{\parallel, \perp}(\omega) = \int_0^\infty dr \phi_{v=0}(r) \alpha_{\parallel, \perp}(r; \omega) \phi_{v=0}(r)$, where $\alpha_{\parallel, \perp}(r; \omega)$ are the radial electronic polarizabilities. Consequently, the eigenenergies of $H_0 + H_{\text{pol}}$ have a linear dependence on I_{trap} , the polarizability of pendular states is independent of laser intensity, and the so-called higher-order hyperpolarizabilities are zero. In Ref. [13] some of us showed the existence of a *magic* angle, where the polarizability is insensitive to laser-intensity fluctuations. This occurs when $C_{20}(\psi_m, 0) = (3 \cos^2 \psi_m - 1)/2 = 0$ or, equivalently, $\psi_m \approx 54^\circ$.

III. THE $^{23}\text{Na}^{40}\text{K}$ DIMER

We can now investigate the energies and polarizabilities of rotational-hyperfine states in the $v = 0$ vibrational level of the $X^1\Sigma^+$ electronic potential of $^{23}\text{Na}^{40}\text{K}$. Its rotational constant is $B_{v=0}/h = 2.8217297(10)$ GHz [23, 27], where h is Planck's constant. The electric dipole moment $d_{v=0} = 1.07(2)ea_0$ [23, 27], where e is the electron charge and a_0 is the Bohr radius. One standard deviation systematic and statistical uncertainties are given in parenthesis. The nuclear spins are 3/2 and 4 for ^{23}Na and ^{40}K , respectively. The nuclear electric quadrupole coupling constants are $(eqQ)_{\text{Na}}/h = -0.187(35)$ MHz and $(eqQ)_{\text{K}}/h = 0.899(35)$ MHz [23]. The two nuclear gyromagnetic ratios are $g_{\text{Na}} = 1.477388(1)$ and $g_{\text{K}} = -0.32406(6)$ [28]. The frequency-dependent dynamic parallel and perpendicular polarizabilities have been computed by us. A brief account of our method as well as numerical values are given in Sec. III A.

A word on energy scales is already in order. The hyperfine and Zeeman interactions as well as H_{pol} have energies (in units of the Planck constant) well below the MHz range as long as the magnetic field strength is below 0.1 T and the laser intensity is no larger than 10^4 W/cm 2 .

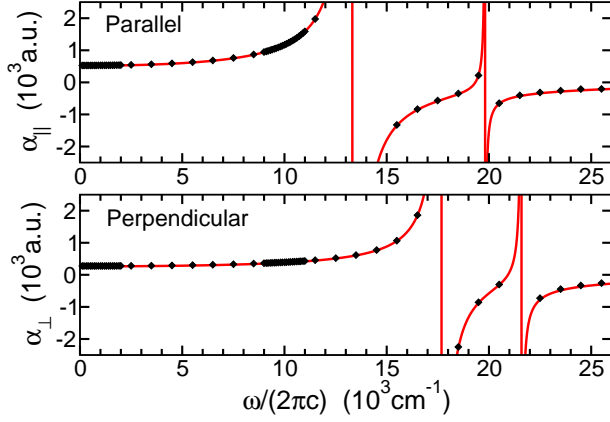


FIG. 1. Dynamic parallel (top panel) and perpendicular (bottom panel) polarizabilities in atomic units, $\text{a.u.}=(ea_0)^2/E_h$, at the equilibrium separation of the ground $X^1\Sigma^+$ electronic state of NaK as functions of laser frequency ω . Black markers are our computed data points, while the solid red curve corresponds to a fit to this data as described in the text. The data is mainly localized near zero frequency and $\omega/(2\pi c) \approx 10000 \text{ cm}^{-1}$. The latter corresponds to laser frequencies typically used for trapping of ultra-cold molecules.

These energy scales are much smaller than B_v as well as DC Stark shifts induced by reasonable electric fields. In order to limit our parameter space the magnetic field $\mathbf{B} = B_z \hat{z}$ with $B_z = 8.57 \text{ mT}$ throughout. This value was used by Park *et al.* [24], who formed weakly-bound Feshbach molecules at this field before performing a two-photon transition to create ground-state molecules. If not otherwise specified, the laser intensity $I_{\text{trap}} = 2.35 \text{ kW/cm}^2$, typical for ultracold experiments.

There are 36 hyperfine states in each rotational manifold $|N, m\rangle$. For electric fields up to 10 kV/cm , rotational hyperfine states with N up to $N_{\text{max}} = 5$ are incorporated in our numerical calculations.

A. Parallel and perpendicular polarizabilities

The dynamic parallel and perpendicular radial electronic polarizabilities $\alpha_{\parallel}(r; \omega)$ and $\alpha_{\perp}(r; \omega)$ can be expressed in terms of a sum over all excited $^1\Sigma^+$ and $^1\Pi$ electronic potentials, respectively. We have calculated these potentials and dynamic polarizabilities of NaK using the CCSD method of the *ab-initio* non-relativistic electronic structure package CFOUR [29]. Relativistic corrections are small for the relatively light Na and K atoms. The def2-QZVPP basis sets of Ref. [30] are used for both atoms and include polarization functions. The specific contraction of primitive basis functions are $(20s\ 12p\ 4d\ 2f)/[9s\ 5p\ 4d\ 2f]$ for Na and $(24s\ 18p\ 4d\ 3f)/[11s\ 6p\ 4d\ 3f]$ for K. The computation is made tractable by only correlating valence electrons and electrons from the outer-most closed shell for each atom.

Figure 1 shows the radial electronic $\alpha_{\parallel}(r_e; \omega)$ and

$\alpha_{\perp}(r_e; \omega)$ computed at the equilibrium separation $r_e = 6.59a_0$ of the ground $X^1\Sigma^+$ state as functions of laser frequency ω . The poles in the functions correspond to frequencies that are equal to the energy difference between an excited- and ground-state potential at r_e . Our pole locations are consistent with the potentials found in Ref. [27]. Our calculated data points from zero frequency up to $\omega/(2\pi c) = 30000 \text{ cm}^{-1}$ are well described by

$$\alpha_{\parallel}(r_e; \omega) = \frac{495.192}{1 - (\nu/13322.2)^2} + \frac{21.3802}{1 - (\nu/19813.6)^2}, \quad (5)$$

$$\alpha_{\perp}(r_e; \omega) = \frac{228.684}{1 - (\nu/17683.6)^2} + \frac{34.6618}{1 - (\nu/21595.1)^2}. \quad (6)$$

in units of $(ea_0)^2/E_h$ and $\nu = \omega/(2\pi c)$ in units of cm^{-1} . Here, E_h is the Hartree energy and c is the speed of light. For $\nu < 21000 \text{ cm}^{-1}$ deviations from the calculated radial polarizabilities are no larger than 1% and 4% for the parallel and perpendicular polarizability, respectively, less than the uncertainty of the CCSD calculation.

The polarizability of the $v = 0$ vibrational level is determined by a vibrational average of $\alpha_{\parallel}(r; \omega)$ and $\alpha_{\perp}(r; \omega)$. The radial $v = 0$ wavefunction $\phi_{v=0}(r)$ is spatially localized around r_e and the r -dependence of the radial polarizabilities is small and, hence, to very good approximation $\alpha_{\parallel, \perp}(\omega)$ are equal to the corresponding radial polarizability at r_e . (Note also that the linear dependence of $\alpha_{\parallel, \perp}(r; \omega)$ near $r = r_e$ does not introduce corrections for nearly Gaussian $\phi_{v=0}(r)$.)

We find that the static (i.e. zero frequency) polarizability for the $N = 0, v = 0$ state $[\alpha_{\parallel}(r_e; 0) + 2\alpha_{\perp}(r_e; 0)]/3 = 348(ea_0)^2/E_h$ is in very good agreement with $351(ea_0)^2/E_h$ from Ref. [31]. Furthermore, in most experimental settings molecules are trapped using lasers with photon energies that are well away from electronic transitions. Without loss of generality, we choose a laser with a wavelength of 1064 nm as used by or suggested in Refs. [24, 32]. The two $v = 0$ polarizabilities are then $\alpha_{\parallel} = 1013.4(ea_0)^2/E_h$ or $\alpha_{\parallel}/h = 4.749 \times 10^{-5} \text{ MHz/(W/cm}^2\text{)}$, and $\alpha_{\perp} = 361.46(ea_0)^2/E_h$ or $\alpha_{\perp}/h = 1.694 \times 10^{-5} \text{ MHz/(W/cm}^2\text{)}$.

B. Energy levels and polarizabilities

Figure 2 shows the lowest 144 rotational-hyperfine eigenenergies of $v = 0$ ground-state $^{23}\text{Na}^{40}\text{K}$ as a function of static electric field strength E_x when no trapping laser is present. These levels correspond to 36 states in the $N = 0$ manifold and 108 states in the $N = 1$ manifold. The electric field is directed along our \hat{x} axis. Panel a) shows these eigenenergies on the scale of the rotational splitting, while panel b) shows a blowup focussing on the $N = 1$ manifold for “small” electric fields. We observe that the DC Stark effect dominates over H_{hf} and H_Z for $E_x > 0.1 \text{ kV/cm}$ and states can then be labeled by the pendular labels $\lambda = 0, 1$ and $|m|$. When the electric field is near zero, pendular states of the same λ with different

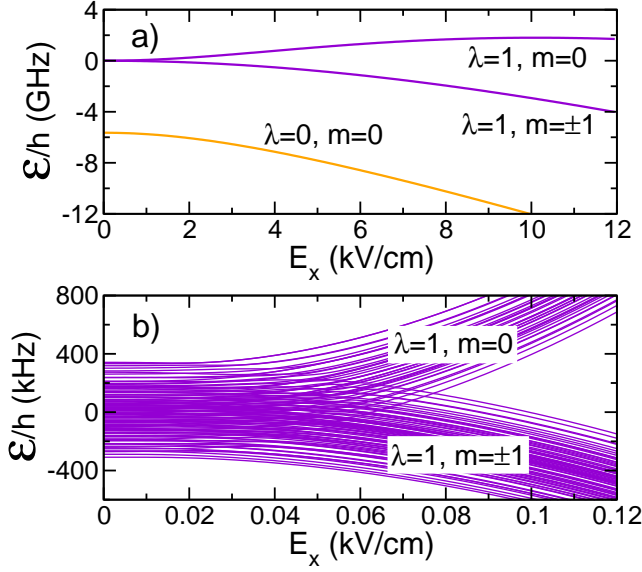


FIG. 2. Eigenenergies of the lowest rotational-hyperfine states of the $v = 0$ vibrational level of the electronic ground-state of $^{23}\text{Na}^{40}\text{K}$ as a function of static electric field strength E_x when no trapping laser is present and $B_z = 8.57$ mT. The electric field $\mathbf{E} = E_x \hat{x}$ is directed along our \hat{x} axis. Panels a) and b) show the same data on two different energy and electric field scales. Approximate labels λ and m valid for large electric fields are indicated. The zero of energy is at the hyperfine barycenter of the $N = 1$ rotational state when $E_x = 0$.

$|m\rangle$ are mixed by H_{hf} and H_Z and the $N = 1$ or equivalently $\lambda = 1$ manifold has a complex level structure.

Figure 3 shows the dynamic polarizabilities $\alpha_{\text{dyn},i}$ of the 144 hyperfine states in the $N = 0$ and 1 manifolds for small electric field strengths, ranging from 0 kV/cm to 0.09 kV/cm, as functions of θ , the angle between the laser polarization and magnetic field direction. The laser has a wavelength of 1064 nm and $I_{\text{trap}} = 2.35$ kW/cm². The magnetic field $B_z = 8.57$ mT and the electric field is applied along either the \hat{z} or \hat{x} direction.

At zero applied electric field, $\alpha_{\text{dyn},i}$ of the 36 hyperfine states in the $N = 0$ manifold are independent of θ . In fact, the total polarizability is given by [16, 33]

$$\alpha_{|N=0,m=0\rangle}(\omega) = (\alpha_{\parallel}(\omega) + 2\alpha_{\perp}(\omega))/3. \quad (7)$$

On the other hand, the polarizability of states in the $N = 1$ manifold behave almost chaotically and is a consequence of strong mixing between the three m . Thus, a small fluctuation in the direction of the polarization will greatly change the trapping potentials for these latter states. Also, each of the corresponding eigenvectors changes drastically with a change in θ , making it difficult to focus on one eigenstate when the directions of external fields change with respect to each other during an experiment. This *non-adiabatic* admixing is due to the fact that the magnetic field is relatively small, and the splitting between states that have similar hyperfine character

but different m are comparable to H_{pol} .

When an electric field is applied, the polarizability of $N = 0$ or $\lambda = 0$ hyperfine states remain independent of θ . The polarizability of the $\lambda = 1$ hyperfine states gradually group, where the polarizability of eigenstates dominated by $m = 0$ character start to coalesce into a single line on the scale of the panels in Fig. 3. The polarizability of $m = \pm 1$ states also simplifies but remains a fairly complex for θ close to zero or 90 degrees. This transition in behavior coincides with the separation of eigenstate energies for states $|\lambda = 1, m = 0\rangle$ from those with $|\lambda = 1, m = \pm 1\rangle$, as depicted by Fig. 2b).

A comparison of the polarizability for electric fields along the \hat{z} and \hat{x} direction and strengths larger than 0.06 kV/cm shows that the natural quantization axis is along the electric field direction. One manifestation is that the $\alpha_{\text{dyn},i}$ for a field along the \hat{x} and \hat{z} axis resemble each other when θ is replaced by $90^\circ - \theta$. I.e. for large fields the angular dependence of $\alpha_{\text{dyn},i}$ only depends on the angle between the laser polarization and electric field. On the other hand the reflection symmetry is not exact. The grouping of the lines of $\alpha_{\text{dyn},i}$ is not the same for the same $|\mathbf{E}|$, due to the remaining competition between the Zeeman and DC Stark Hamiltonians. For example, the 36 $\alpha_{\text{dyn},i}$ of states in the $|\lambda = 1, m = 0\rangle$ manifold in Fig. 3f) are more spread out than those in Fig. 3c).

C. Single- and double-magic conditions

A careful study of Figs. 3c and 3f shows that *magic* conditions are starting to occur. With the electric field along the \hat{z} axis and $E_z = 0.09$ kV/cm the polarizabilities α_{dyn} of hyperfine states in the $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ manifolds are almost the same near $\theta = 54.7^\circ$ (or equivalently near $\psi_m = 54.7^\circ$). This occurs regardless of the hyperfine state in either manifold. Moreover, for an electric field along the \hat{x} axis *magic* conditions occur for $\theta \approx 90^\circ - 54.7^\circ \approx 35.3^\circ$.

We study this coalescence of the polarizabilities in more detail for much larger electric field strengths and locate a case of double *magic* conditions. Figure 4 shows the polarizability of states in the $\lambda = 0$ and 1 manifolds for electric fields $E_x = 2.0$ kV/cm, 5.265 kV/cm, and 8.0 kV/cm along the \hat{x} axis. The polarizability of the $|\lambda = 0, 1, m = 0\rangle$ hyperfine states has now fully collapsed into one of two θ -dependent curves. In fact, these $m = 0$ polarizabilities are equal to better than 0.01 % for both $\lambda = 0$ and 1 hyperfine manifolds. For the smallest and largest of the three strong electric fields the $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ curves cross at the *magic* angle 54.7° . Crucially, for the *magic* intermediate electric field strength of 5.265 kV/cm, shown in Fig. 4b), the polarizabilities of all hyperfine state of the $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ manifolds coincide throughout the *entire* range of θ . In fact, this *magic* electric field strength exists regardless of field direction.

The dynamic polarizability of the $|\lambda = 1, m = \pm 1\rangle$

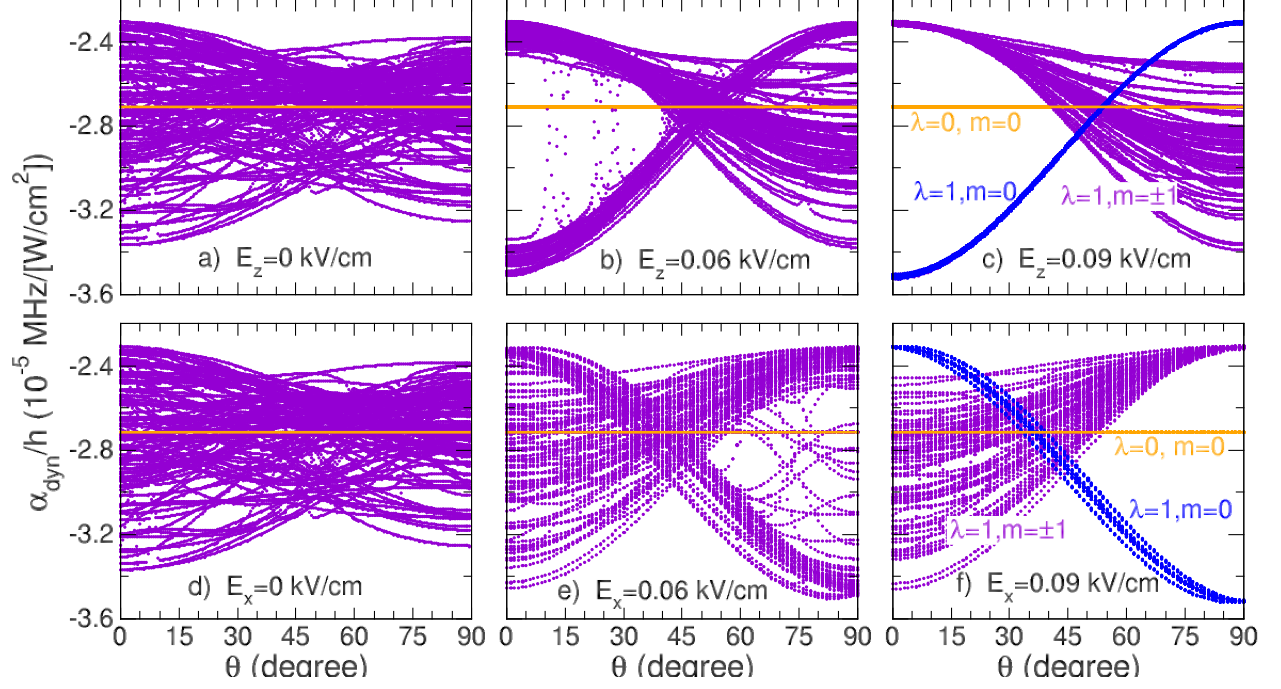


FIG. 3. Dynamic polarizabilities of the lowest 144 eigen states of $^{23}\text{Na}^{40}\text{K}$ as functions of the angle θ at small electric fields, $|\mathbf{E}| = 0$ kV/cm, 0.06 kV/cm, and 0.09 kV/cm. Panels on the top and bottom row correspond to an electric field along the \hat{z} and \hat{x} axis, respectively. In panels a), b), d), and e) the orange line and purple markers correspond to $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = \pm 1\rangle$ hyperfine states, respectively. In panels c) and f) the orange, blue, and purple lines and markers correspond to $|\lambda = 0, m = 0\rangle$, $|\lambda = 1, m = 0\rangle$, and $|\lambda = 1, m = \pm 1\rangle$ hyperfine states, respectively. Panels a) and d) for zero electric field are identical. The copy is only included for easy comparison with other panels. We use $B_z = 8.57$ mT, a laser wavelength of 1064 nm, and $I_{\text{trap}} = 2.35$ kW/cm 2 .

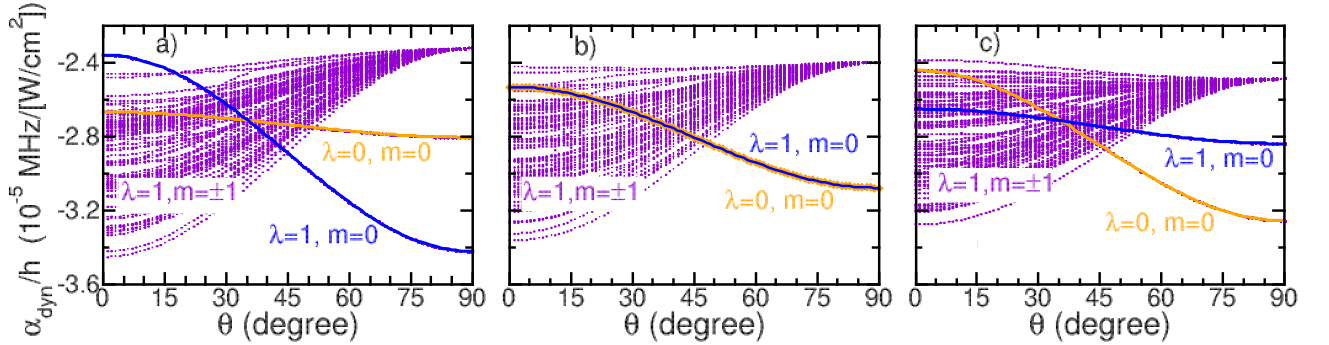


FIG. 4. Dynamic polarizabilities of the lowest 144 rotational-hyperfine states of the ground vibrational level of $^{23}\text{Na}^{40}\text{K}$ as functions of the angle θ for three strong electric fields $\mathbf{E} = E_x \hat{x}$ with $E_x = 2.0$ kV/cm, 5.265 kV/cm, and 8.0 kV/cm in panel a), b), and c), respectively. Orange, blue, and purple lines and markers correspond to hyperfine states in the $|\lambda = 0, m = 0\rangle$, $|\lambda = 1, m = 0\rangle$, and $|\lambda = 1, m = \pm 1\rangle$ manifolds, respectively. We use $B_z = 8.57$ mT, a laser wavelength of 1064 nm, and $I_{\text{trap}} = 2.35$ kW/cm 2 .

hyperfine states remains very state dependent regardless of the electric field strength. Here, the hyperfine and Zeeman interactions lead to ever changing couplings between the nearly-degenerate $m = \pm 1$ states and, thus, to changing dynamic polarizabilities as functions of electric field and angle.

Figure 5 shows the dynamic polarizabilities of the $m = 0$ hyperfine states of $^{23}\text{Na}^{40}\text{K}$ but now as functions of electric field strength for eleven angles θ . The field is directed along the \hat{x} axis. We see that for all angles the $\lambda = 0$ and 1 polarizabilities cross at $E_x = 5.265$ kV/cm. At the special angle of $\theta = 35.3^\circ$ these polarizabilities

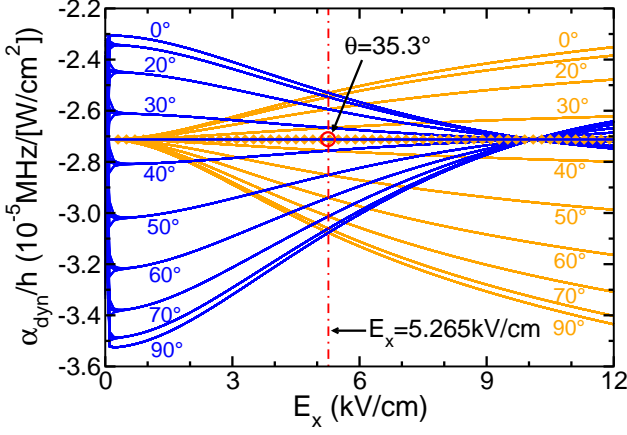


FIG. 5. Dynamic polarizabilities of $m = 0$ rotational-hyperfine states of the ground vibrational level of $^{23}\text{Na}^{40}\text{K}$ as functions of the strength of an applied electric field for the eleven angles $\theta = 0^\circ, 10^\circ, \dots, 80^\circ, 90^\circ$ and 35.3° . The electric field is directed along the \hat{x} axis. Orange dashed and blue solid lines are polarizabilities for hyperfine states of the $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ manifold, respectively. For $\theta = 35.3^\circ$ the polarizability for the two manifolds is the same and independent of E_x . At the red circle where $\theta = 35.3^\circ$ and $E_x = 5.265$ kV/cm our double *magic* condition holds. We use $B_z = 8.57$ mT, a laser wavelength of 1064 nm, and $I_{\text{trap}} = 2.35$ kW/cm 2 .

are the same for *any* electric field $|\mathbf{E}| > 0.25$ kV/cm. The red circle on this line corresponds to $|\mathbf{E}| = 5.265$ kV/cm and a double *magic* condition where both the angular and electric field *magic* conditions are met. In fact, this double *magic* condition exists regardless of the field direction. It occurs when the angle between the direction of the laser polarization and the direction of the electric field is $\psi_m = 54.7^\circ$ and $|\mathbf{E}| = 5.265$ kV/cm. Under normal fluctuations of experimental conditions, this double *magic* condition provides extra stability for the matching of trapping potentials of hyperfine states in the $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ manifolds. The difference in polarizabilities, $\Delta\alpha_{\text{dyn}}$, near the double magic condition is no more than 0.03%, when the electric field strength and the angle are changed by ± 0.1 kV/cm and $\pm 1^\circ$, respectively. Of course, when only one of $|\mathbf{E}|$ or ψ_m fluctuates, then $\Delta\alpha_{\text{dyn}}$ is an order magnitude smaller.

The same concept does apply to other ultracold dipolar species. The value for the *magic* $|\mathbf{E}|$ will be different, of course, and is determined by the rotational constant, the permanent dipole moment, as well as the radial electronic polarizability.

D. Sensitivity to the laser intensity

A second benefit of applying a strong electric field is the negligible dependence of the dynamic polarizabilities of $m = 0$ hyperfine states on laser intensity, consistent

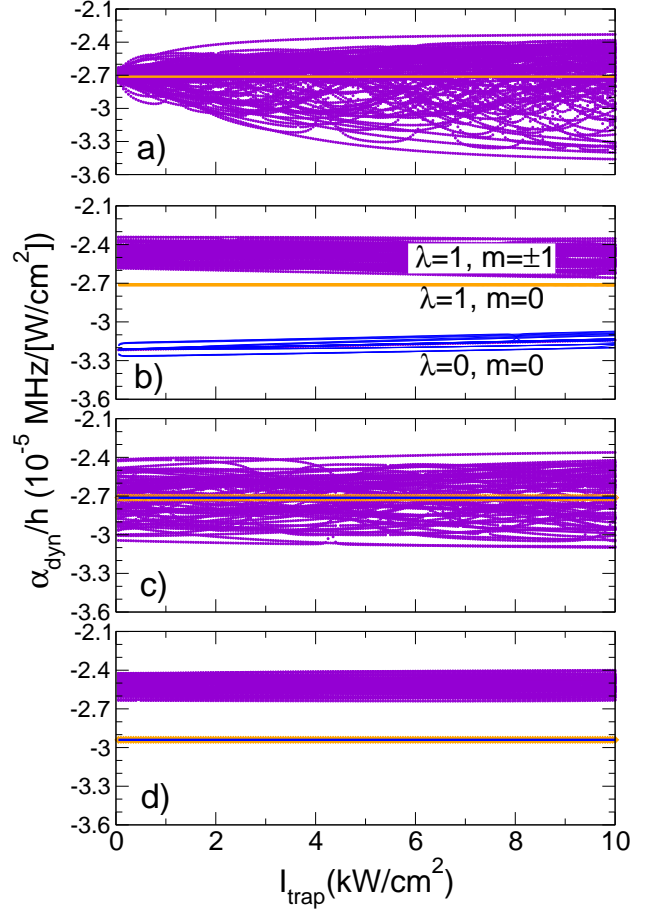


FIG. 6. Dynamic polarizabilities of the lowest 144 eigenstates of the vibrational ground state of $^{23}\text{Na}^{40}\text{K}$ as functions of the trapping laser intensity I_{trap} at four representative pairs $(E_x, \theta) = (0.0, 60^\circ), (0.09, 60^\circ), (2.0, 35.3^\circ)$ and $(5.265, 60^\circ)$ in panels a), b), c) and d), respectively. The electric field is in units of kV/cm and points along the \hat{x} axis. In all panels the orange dashed line corresponds to α_{dyn} of the 36 $\lambda = 0, m = 0$ hyperfine states. In panel a) the purple dots correspond to the 108 $\lambda = 1$ hyperfine states with mixed m character. In panels b), c), and d) the blue and purple dots are eigenstates dominated by $|\lambda = 1, m = 0\rangle$ and (mixed) $|\lambda = 1, m = \pm 1\rangle$ pendular functions. In panels c) and d) the polarizabilities of the $m = 0$ eigenstates are indistinguishable. Both correspond to *magic* conditions for $^{23}\text{Na}^{40}\text{K}$. We use $B_z = 8.57$ mT and a laser wavelength of 1064 nm.

with the prediction of the pendular model in Sec. II C. In Fig. 6, the polarizabilities of the 144 states in the $\lambda = 0$ and 1 manifolds are plotted as functions of laser intensity for four representative pairs (E_x, θ) . When the electric field is small or zero, i.e. $E_x \ll 0.1$ kV/cm, the 108 eigen states in the $\lambda = 1$ manifold are mixed with respect $m = 0, \pm 1$ and are sensitive to fluctuations in the experimental conditions, including that of the trapping laser intensity. Figure 6a shows that the dependence of the polarizabilities of these states on I_{trap} is compli-

cated. Even if the polarizabilities are matched for two states, small fluctuations introduce a mismatch between the polarizabilities and thus the trapping potentials. As the electric field strength is increased to 0.1 kV/cm some states start to be dominated by $m = 0$ character and separated from the others. Their polarizabilities group, as shown in Fig. 6b). As the strength of the electric field is further increased to $E_x \gg 0.1$ kV/cm the polarizabilities of states dominated by $|\lambda = 1, m = 0\rangle$ character coincide and become independent of the intensity. This is demonstrated at the *magic* angle and the *magic* electric field in Figs. 6c) and 6d), respectively, where the polarizabilities of the $|\lambda = 1, m = 0\rangle$ states also equal that of $|\lambda = 0, m = 0\rangle$ states. The polarizabilities of $|\lambda = 1, m = \pm 1\rangle$ states still remain sensitive to laser intensity fluctuations.

We quantify the dependence of the polarizabilities on the intensity with the difference in the hyperpolarizabilities between the $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ states, where the hyperpolarizability of state i is defined as $\beta_i = d\alpha_{\text{dyn},i}/dI_{\text{trap}}$, where the laser-intensity dependence of the electronic hyperpolarizability of $\alpha_{\parallel}(r; \omega)$ and $\alpha_{\perp}(r; \omega)$ can be safely neglected. At the double *magic* condition, the difference between the two hyperpolarizabilities is ~ 0.03 Hz/[kW/cm²]². This implies that a change of the trapping laser intensity of 1 kW/cm² will result in the change of the polarizability by about one part in a million. Hence, the intensity dependence of the total polarizability is insignificant and can be neglected.

IV. SUMMARY

The current study has provided quantitative theoretical information on ultracold polar $^1\Sigma^+$ molecules that can be used to improve control of molecular superposition states and conduct precision frequency measurements. The relevant quantity for controlling molecules with laser fields is the molecular dynamic polarizability as a function of radiation frequency and polarization. Integrated over the laser intensity its real part determines the strength of a trapping or lattice potential. As different ro-vibrational states have different lattice depths or Stark shifts their trapping potential differs. Our goal was to determine a combination of laser-field parameters and DC electric and magnetic fields that ensure identical and strong trapping forces for two internal rotational states and, simultaneously, low sensitivity to field fluctuations.

Understanding the effect of changing the relative orientation, polarization and strength of these three fields is of crucial importance for creation of decoherence-free subspaces built from two or more ro-vibronic and hyperfine states. This research was in direct response to recent experimental advances in creating NaK molecules in their

absolute ground state [4].

We relied on an effective decoupling of rotational and nuclear degrees of freedom of ultracold polar di-atomic molecules. This decoupling can be used to prepare pairs of rotational-hyperfine states that exhibit fluctuation-insensitive *magic* trapping conditions, where two states have the same dynamic polarizability. These *magic* conditions can be either single or double in nature by giving stability against one or two distinct types of fluctuations.

Our theoretical predictions are based on a quantitative Hamiltonian for ro-vibrational, hyperfine states of $^1\Sigma^+$ molecules in the presence of various external electromagnetic fields. These include a magnetic field, the static electric field, and trapping laser fields. Among them, the electric field is especially useful in simplifying the theory for states dominated by the rotational projection quantum number $m = 0$ and, thereby, leads to our hyperfine-state insensitive *magic* trapping conditions. This simplified theory leads to pendular states and the physical intuition of our results.

We studied the electronic ground-state $^{23}\text{Na}^{40}\text{K}$ molecule as an important test case. The results, however, can be easily transferred to other $^1\Sigma^+$ molecules. We used the newly calculated parallel and perpendicular electronic dynamic polarizabilities of $^{23}\text{Na}^{40}\text{K}$. For strong electric fields a *magic* angle of $\psi_m = 54.7^\circ$ is found, which protects against fluctuations in the angle between the laser polarization and electric field for the 72 hyperfine states with $|\lambda = 0, m = 0\rangle$ and $|\lambda = 1, m = 0\rangle$ character. We also predict the existence of a double *magic* condition at an electric field strength of 5.26(15) kV/cm and angle $\phi_m = 54.7^\circ$. It provides stability against electric field strength fluctuations. For these $m = 0$ hyperfine states the laser-intensity dependence of the dynamic polarizabilities is shown to be insignificant. The one-standard deviation uncertainty of the *magic* electric field is due to the combined uncertainty of the permanent electric dipole moment and the parallel and perpendicular electronic polarizabilities.

For $|m| = 1$ hyperfine states the dynamic polarizability shows complex angle, field strength and intensity dependence due the near energy degeneracy of these states independent of electric field strength. Under these circumstances (double) *magic* conditions between one $m = 0$ and one $|m| = 1$ state or between two $|m| = 1$ states seems unlikely or, at least, system dependent.

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