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Manipulating ultracold polar molecules with microwave radiation: The influence of hyperfine structure

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We calculate the microwave spectra of ultracold $^{40}\text{K}^{87}\text{Rb}$ alkali-metal dimers, including hyperfine interactions and in the presence of electric and magnetic fields. We show that microwave transitions may be used to transfer molecules between different hyperfine states, but only because of the presence of nuclear quadrupole interactions. Hyperfine splittings may also complicate the use of ultracold molecules for quantum computing. The spectrum of molecules oriented in electric fields may be simplified dramatically by applying a simultaneous magnetic field.

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Ultracold molecules offer striking new possibilities in many areas of science [1]. The novel applications include the development of quantum control schemes using electric and magnetic fields, the employment of ultracold molecules in quantum-information storage and processing, the production of strongly interacting quantum gases and the possibility of performing precision measurements of physical quantities [2].

It has been possible since 2003 to produce alkali-metal dimers in highly excited vibrational states in ultracold atomic gases [3]. However, it is only in the last year that it has been possible to transfer these molecules coherently to deeply bound states. This has now been achieved for K₂ [4], Cs₂ [5–7] and triplet Rb₂ [8]. RbCs [9], LiCs [10], and NaCs [11] have also been prepared in deeply bound states, but so far by incoherent methods.

The bound states of diatomic molecules are described by vibrational and rotational quantum numbers v and N . However, this does not suffice to specify the state completely, as most molecules also possess complicated hyperfine structure [12,13], even for singlet molecules in $N=0$ states [14,15]. This structure cannot be neglected in ultracold studies, both because hyperfine energy splittings can be of the same order of magnitude as the thermal energy and because the molecules must be in the same hyperfine state to achieve Bose-Einstein condensation or Fermi degeneracy.

The interaction of cold molecules with microwave fields plays a central role in proposals for microwave traps [16,17], for tuning molecule-molecule interactions to form novel quantum phases [18–20], for studying the dynamics of quantum phase transitions [21,22] and for the employment of ultracold molecules in quantum computing [21,23,24]. The goal of this work is to show that the hyperfine structure of microwave molecular spectra is important in experiments involving cold and ultracold molecules.

In the present work, we simulate the microwave spectrum of an alkali-metal dimer including hyperfine interactions and

in the presence of electric and magnetic fields. We consider $^{40}\text{K}^{87}\text{Rb}$ in the ground electronic state ($^1\Sigma^+$), which has been experimentally prepared in the ground rovibrational state ($v=0$, $N=0$) by Ni *et al.* [4]. However, the spectra of other alkali-metal dimers will display very similar features. We demonstrate the importance of the hyperfine structure by discussing (i) how microwave transitions can be used to transfer molecules between hyperfine states and (ii) the consequences of hyperfine structure for the use of ultracold polar molecules in quantum computing according to the scheme proposed by DeMille [23].

The first step in the experiment of Ni *et al.* [4] is to form $^{40}\text{K}^{87}\text{Rb}$ dimers in a high-lying vibrational state from the corresponding ultracold atoms. This is accomplished by tuning the magnetic field across a Feshbach resonance. The resulting dimers are characterized by a projection of the total angular momentum on the direction of the field $M_F=-7/2$. They are then transferred into the ground rovibrational state using STIRAP (STImulated Raman Adiabatic Passage) [25]. The transfer is carried out at a magnetic field $B=545.9$ G. The polarization of the lasers is such that M_F is conserved during the STIRAP transfer. We therefore concentrate here on the $M_F=-7/2$ levels for $v=0$, $N=0$ and 1, although by selecting a different initial state and/or by changing the polarization of the STIRAP lasers it would be possible in principle to populate different hyperfine states.

The molecular Hamiltonian of a $^1\Sigma$ molecule in the presence of external fields can be written [13–15]

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

where H_{rot} , H_{hf} , H_S and H_Z represent the rotational, hyperfine, Stark and Zeeman contributions, respectively. We construct and diagonalize the Hamiltonian matrix in an uncoupled basis set $|N, M_N\rangle |I_K M_K\rangle |I_{\text{Rb}} M_{\text{Rb}}\rangle$, where N is the molecular rotational angular momentum and $I_K=4$ and $I_{\text{Rb}}=3/2$ are the nuclear spins. M_N , M_K , and M_{Rb} are the projection quantum numbers for N , I_K , and I_{Rb} on the axis defined by the magnetic field. If the electric and magnetic fields are parallel, the total projection $M_F=M_N+M_K+M_{\text{Rb}}$ is a good quantum number. Since I_K and I_{Rb} are fixed, we ab-

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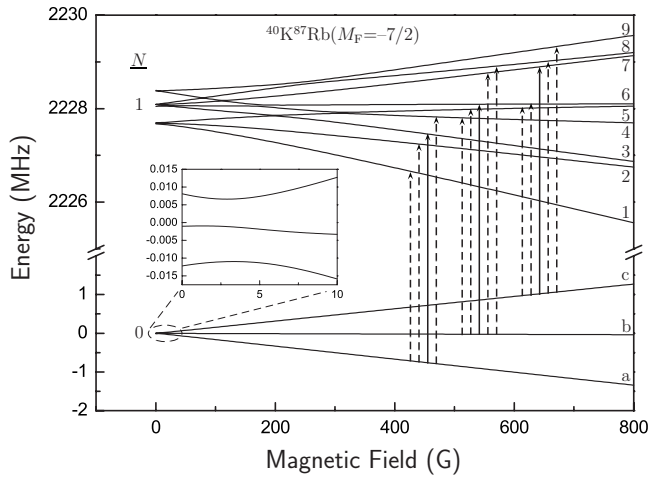


FIG. 1. Hyperfine and Zeeman energy levels for $M_F = -7/2$ states of $^{40}\text{K}^{87}\text{Rb}$ ($v=0$, $N=0-1$) in zero electric field. The more probable microwave transitions from $N=0$ (a)–(c) to $N=1$ (1)–(9) states at a magnetic field $B=545.9$ G are indicated with arrows (see Fig. 2 for more details). Although all the arrows correspond to transitions at $B=545.9$ G, they have been displaced in order to make visualization easier. Continuous lines represent the most probable transition for each $N=0$ state. The small panel contains a blow-up of the $N=0$ levels for values of the magnetic field below 10 G.

breviate the basis functions to $|N, M_N, M_K, M_{\text{Rb}}\rangle$. The matrix elements of the various terms in the Hamiltonian and of the transition dipole operator in this basis set are obtained by standard angular momentum techniques [14,26].

The hyperfine and Zeeman Hamiltonians consist of several terms whose coupling constants have been evaluated using DFT calculations with relativistic corrections: see reference [14] for details of the methods used for the calculation of the coupling constants. The Stark Hamiltonian is evaluated using the experimental value of the KRb dipole moment, $\mu=0.566$ D [4].

The hyperfine and Zeeman splitting for the $M_F = -7/2$ states of $^{40}\text{K}^{87}\text{Rb}$ ($N=0$ and 1) in zero electric field is shown in Fig. 1. All the apparent crossings between energy levels are avoided crossings. Three terms in the Hamiltonian (apart from H_{rot}) determine the main features of this figure: the scalar nuclear spin-spin, nuclear electric quadrupole, and nuclear Zeeman interactions [14,15]. For the $N=0$ levels, the zero-field splitting arises from the scalar part of the electron-mediated interaction between the magnetic moments of the nuclei, characterized by coupling constant $c_4 = -2.0304$ kHz. The zero-field splitting amounts to 20 kHz, as shown in the small panel in Fig. 1. For the $N=1$ levels, the zero-field splitting is mainly due to the nuclear electric quadrupole term, with coupling constants $(eQq)_{^{40}\text{K}} = 0.306$ MHz and $(eQq)_{^{87}\text{Rb}} = 1.520$ MHz, and amounts to approximately 1 MHz. This term, which describes the interaction between the nuclear quadrupole moments and the electric field gradient created by the electrons at the nuclear positions, is much larger than the scalar spin-spin interaction for $^{40}\text{K}^{87}\text{Rb}$ and most of the other alkali-metal dimers. It generally dominates the zero-field splitting except for $N=0$

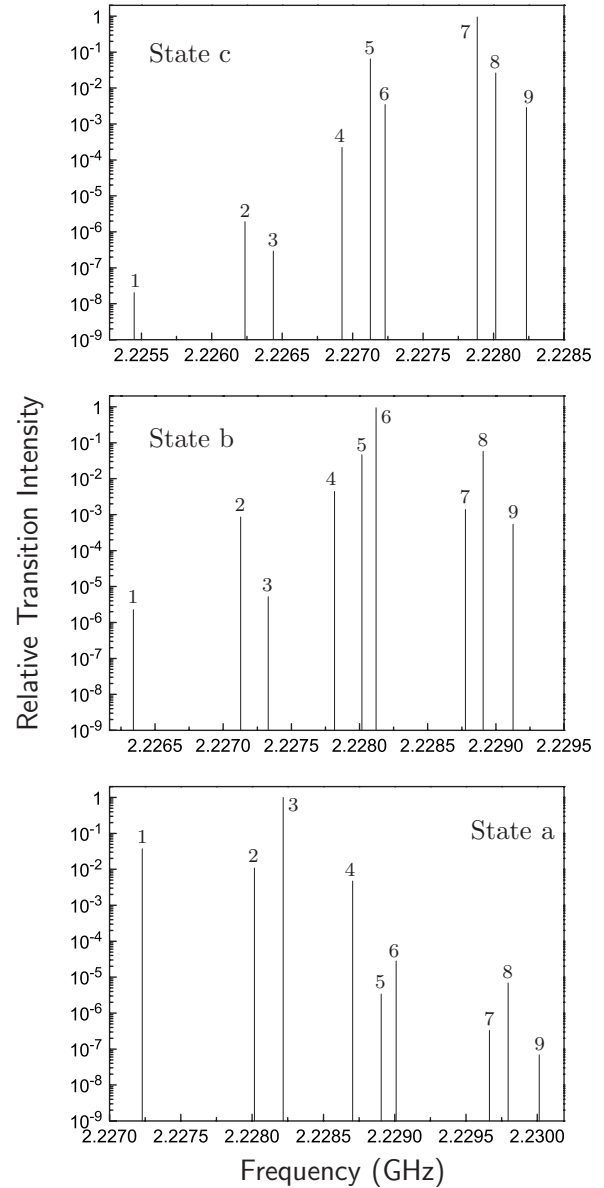


FIG. 2. Relative probability for the $^{40}\text{K}^{87}\text{Rb}$ ($v=0$, $M_F = -7/2$) microwave transitions from $N=0$ to $N=1$ hyperfine states at $B=545.9$ G and zero electric field. The transitions shown here are for microwave radiation polarized parallel to the magnetic field, so have $\Delta M_F = 0$. Each panel contains all the transitions from one of the three $N=0$ hyperfine states, labeled as a (bottom), b (middle) and c (top). The $N=1$ states are labeled 1 to 9. The process with the largest transition dipole moment (peak 3 in the bottom panel) has been assigned an intensity of 1 and all the other transitions are relative to it.

because the matrix elements of the nuclear electric quadrupole Hamiltonian between $N=0$ basis functions vanish. The main contribution to the Zeeman Hamiltonian comes from the interaction between the nuclear magnetic moments and the magnetic field (nuclear Zeeman effect). Other terms, such as the tensor nuclear spin-spin, nuclear spin-rotation and rotational Zeeman interactions, are much less significant.

It is important to develop methods to control the hyperfine states of ultracold molecules. It may be possible to use mi-

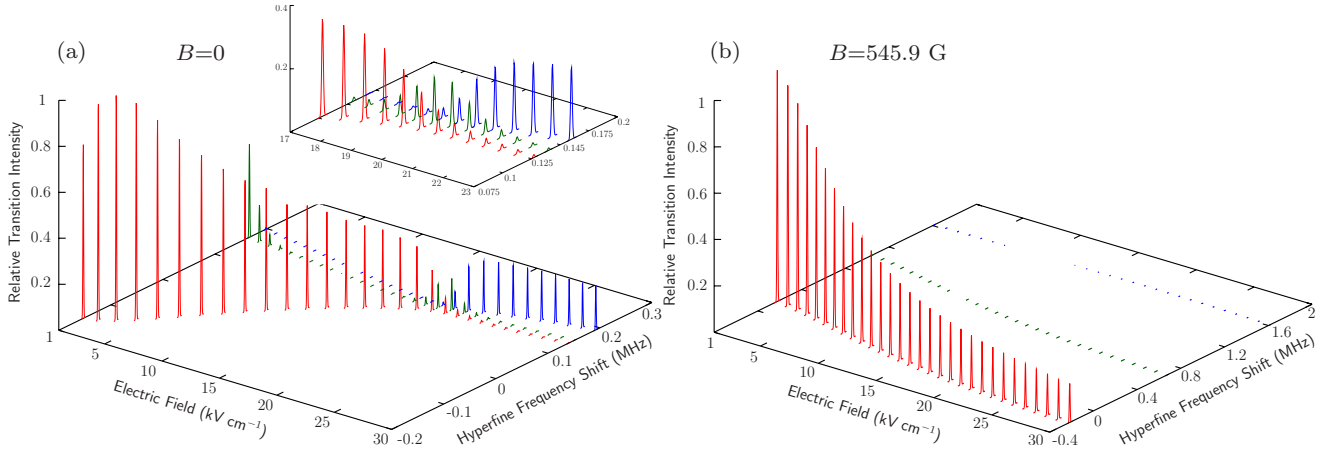


FIG. 3. (Color online) Relative intensities of the microwave transitions from the lowest $v=0$, $N=0$ hyperfine state of $^{40}\text{K}^{87}\text{Rb}$ to the three possible $N=1$, $M_N=0$ hyperfine states, as a function of the external electric field, (a) in the absence of a magnetic field and (b) in the presence of a parallel magnetic field $B=545.9$ G. All levels have $M_F=-7/2$. The microwave field is polarized parallel to the fields. The inset shows an enlargement of the crossing region in (a). The most intense transitions in (a) and (b) have been assigned a peak intensity of 1. In order to keep the spectrum on a single frequency scale as a function of electric field, we plot the hyperfine frequency shift instead of the absolute frequency. This is obtained by subtracting the frequency for the transition in the absence of hyperfine splittings.

crowave transitions between $N=0$ and $N=1$ levels to transfer alkali-metal dimers between different hyperfine states, as has been done for cold ND_3 and OH molecules [27,28]. In order to establish whether this is feasible, we simulate the microwave spectrum for all three $N=0$ hyperfine states of $^{40}\text{K}^{87}\text{Rb}$ with $M_F=-7/2$. We evaluate the transition dipole moments of the relevant transitions in the presence of a magnetic field $B=545.9$ G. The relative intensities for a microwave field polarized parallel to the magnetic field are shown in Fig. 2. Numerical values of the level energies and intensities for both parallel and nonparallel polarization are available as supplementary material [29]. For each of the $N=0$ hyperfine states, there are several transitions with intensity within a factor of 10^3 of that of the strongest transition, highlighted with arrows in Fig. 1. Some of the $N=1$ hyperfine states can be reached with significant intensity from more than one $N=0$ state. Microwave radiation with a polarization that is not parallel to the magnetic field can also drive transitions with $\Delta M_F \neq 0$. It will therefore be possible to use microwave transitions to transfer ultracold alkali-metal dimers between hyperfine states, including to the $M_F=-5/2$ absolute ground state.

It is important to note that the transfer would *not* be possible in the absence of nuclear quadrupole interactions. If the quadrupole terms are omitted, the subsidiary transitions in Fig. 2 have intensities at least six orders of magnitude less than that of the main peaks. The selection rules for transitions driven by a z -polarized microwave field are $\Delta N = \pm 1$, $\Delta M_N = 0$, $\Delta M_K = 0$, and $\Delta M_{\text{Rb}} = 0$ in the uncoupled basis set. At $B=545.9$ G, the $N=0$ block of the Hamiltonian is dominated by the nuclear Zeeman term, which is diagonal in this basis set. The only interactions that couple $N=0$ to higher N are small hyperfine terms. Because of this, M_N , M_K , and M_{Rb} are nearly good quantum numbers for $N=0$. If this were also the case for the $N=1$ levels, only one transition from each initial state,

$$|N=0, M_N=0, M_K, M_{\text{Rb}}\rangle \rightarrow |N=1, M_N=0, M_K, M_{\text{Rb}}\rangle, \quad (2)$$

would have significant intensity in Fig. 2. However, the electric quadrupole interaction prevents this: it is off-diagonal in the uncoupled basis set for $N=1$ and strongly mixes the $|N=1, M_N, M_K, M_{\text{Rb}}\rangle$ basis functions. Since the projection quantum numbers are not well defined for $N=1$, the selection rules involving them are less restrictive.

Hyperfine structure will also be important in applications of ultracold molecules to quantum computing. DeMille [23] has proposed a design for a quantum computer in which the qubits are formed from ultracold polar molecules held in a one-dimensional (1D) optical lattice. Each of the trap sites (10^4 in the original design) is occupied by a single molecule. To facilitate individual addressing, an external electric field ϵ that varies linearly with the position in the array is applied. The $|0\rangle$ and $|1\rangle$ states of the qubits are field-induced mixtures of the $M_N=0$ rotational states, characterized by orientations of the molecular electric dipole parallel and antiparallel to the electric field, respectively. At the fields where the device operates, $|0\rangle$ is predominantly $N=0$ and $|1\rangle$ is predominantly $N=1$. Switching between the $|0\rangle$ and $|1\rangle$ states is driven by microwave fields whose polarization is parallel to ϵ ($\Delta M_F=0$).

In DeMille's design, the qubits are KCs molecules. When the original experimental parameters are adapted to use KRb, the optimum range for the external electric field is from approximately 7 to 18 kV/cm and the electric resonance frequencies needed to address the molecules range from 3.5 to 6 GHz in steps of 250 kHz.

The ultracold dimers will properly represent qubits only if it is possible to switch repeatedly between the $|0\rangle$ and $|1\rangle$ states of one molecule without populating other states and without modifying the state of any other molecule during the process. The existence of several possible hyperfine transi-

tions can complicate the operation of the device by making the individual addressing of molecules more difficult.

In order to determine the extent of these difficulties, we simulate the microwave spectrum for transitions from the lowest $N=0$ hyperfine state of KRb in an electric field. Even an electric field as small as 0.5 kV/cm is sufficient to separate the levels for $M_N=0$ and ± 1 . Figure 3(a) shows the hyperfine frequency shifts and intensities for transitions to the three $N=1$, $M_N=0$ levels for $M_F=-7/2$, calculated for electric fields between 1 and 30 kV/cm in the absence of a magnetic field. The peaks display a crossing as a function of the electric field ϵ . The crossing region, corresponding to values of ϵ between 17 and 23 kV/cm, is shown in the inset of Fig. 3(a). It is characterized by the existence of three significant peaks for each value of the field. The behavior of the peaks reflects that of the $N=1$, $M_N=0$ hyperfine levels, which display avoided crossings in the same range of electric fields. Even outside the crossing region, all three peaks have significant intensities (mostly $\geq 10^{-4}$ of that of the main peak).

Hyperfine splittings will thus complicate the individual addressing of molecules in a quantum computer based on DeMille's design [23]. For electric fields between 7 and 15 kV/cm, the peaks spread over a range of frequency shifts that is comparable to or larger than the frequency step used for addressing (250 kHz). This may cause overlapping between the spectra of neighboring molecules.

This difficulty can be overcome by applying a magnetic field parallel to the electric field. The magnetic field resolves

the near-degeneracy between levels with different values of M_K and M_{Rb} but the same M_F . The spectrum calculated for $B=545.9$ G (the magnetic field value in the experiment of Ni *et al.* [4]) is shown in Fig. 3(b). A single transition dominates the spectrum for all values of the electric field and no crossing is displayed. The subsidiary transitions are seven or eight orders of magnitude weaker than the primary transition.

It is thus clear that a detailed understanding of hyperfine structure is essential when designing experiments that involve microwave transitions in ultracold molecules. We have shown that microwave transitions could be used to transfer polar molecules between hyperfine states, but only because of the presence of the nuclear electric quadrupole interaction. We have also investigated the possibility of using ultracold polar molecules as the basis for the logic gates of a quantum computer. In this case the hyperfine splittings introduce some difficulties in the operation of the device, but these can be overcome by applying a magnetic field as well as an electric field.

Note added. Recently, Ospelkaus *et al.* [30] succeeded in using microwave transitions to transfer molecules between the $N=0$ hyperfine states of $^{40}\text{K}^{87}\text{Rb}$.

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