Multi-channel modelling of the formation of vibrationally cold polar KRb molecules

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Abstract. We describe the theoretical advances that influenced the experimental creation of vibrationally and translationally cold polar $^{40}\text{K}^{87}\text{Rb}$ molecules [1, 2]. Cold molecules were created from very-weakly bound molecules formed by magnetic field sweeps near a Feshbach resonance in collisions of ultra-cold $^{40}\text{K}$ and $^{87}\text{Rb}$ atoms. Our analysis include the multi-channel bound-state calculations of the hyperfine and Zeeman mixed $^{\Sigma_{1}^+}$ and $^{3\Sigma_{1}^+}$ vibrational levels. We find excellent agreement with the hyperfine structure observed in experimental data. In addition, we studied the spin–orbit mixing in the intermediate state of the Raman transition. This allowed us to investigate its effect on the vibrationally averaged transition dipole moment to the lowest rovibrational level of the $^{\Sigma_{1}^+}$ state. Finally, we obtained an estimate of the polarizability of the initial and final rovibrational states of the Raman transition near frequencies relevant for optical trapping of the molecules.

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1. Introduction

The recent successful creation of a high phase-space-density gas of polar $^{40}\text{K}^{87}\text{Rb}$ molecules \cite{1, 2} has been based on both new experimental and theoretical advances in manipulating and understanding properties of such molecules. This opens up the possibility of studying collective phenomena that rely on the long-range interactions between polar molecules. Future experiments can be envisioned in both weakly confining optical traps as well as optical lattices.

Our goal in this paper is to describe some of the theoretical advances that influenced the experimental creation of vibrationally and translationally cold polar $^{40}\text{K}^{87}\text{Rb}$ molecules. In particular, we theoretically analyze various factors that can affect this creation including the multi-channel description of the initial, intermediate and final states of the formation by Raman transitions.

In a previous paper \cite{3}, we made the first steps toward obtaining practical guidelines for photoassociatively producing low $v$ vibrational states of heteronuclear KRb. We calculated the electronic transition dipole moments between the ground state of the KRb molecule and excited states. In addition, we obtained the permanent dipole moments of the polar $X^1\Sigma^+$ and $a^3\Sigma^+$ ground states. A relativistic electronic structure code was used.

In a second paper \cite{4}, we discussed the possibility of creating $X^1\Sigma^+$ molecules starting from doubly spin-polarized K and Rb atoms via two-photon photoassociation, which converts pairs of colliding atoms into stable molecules. We assumed that colliding atoms are initially in the doubly spin-polarized state, which only allows them to bond in the ground configuration $a^3\Sigma^+$ potential. We then found that there is a viable route from the doubly spin-polarized colliding atoms to the vibrationally ground $X^1\Sigma$ state via the excited $A^1\Sigma^+$ and $b^3\Pi$ states, when they are mixed through spin–orbit interactions. The mixing between these states is significant so that the Hund’s case (c) coupling scheme, where the electron orbital angular momentum and spin are strongly mixed, is valid. This leads to $2(0^+)$ and $3(0^+)$ states and allowed us to calculate the Raman transition rate from the triplet state to the excited $\Omega = 0^+$ state followed by a downward transition to the ground singlet state. Such a process is absent in homonuclear dimers, since the additional gerade-ungerade symmetry prevents it. In the notation $m(\Omega^p)$ the number in parenthesis is the projection $\Omega$ of the total electronic angular momentum on the internuclear axis, $p$ denotes a reflection symmetry when $\Omega = 0$, and the number in front labels the order of states with the same $\Omega$. The role of black-body radiation in redistributing population among rovibrational levels of the singlet $X^1\Sigma^+$ and triplet $a^3\Sigma^+$ states was investigated.

Here, we further search for an efficient production mechanism using a multi-channel description of both ground and excited states. We assume that KRb molecules are initially in the weakly bound near-threshold vibrational states formed by a magnetic Feshbach resonance in collisions between ultracold $^{40}\text{K}$ and $^{87}\text{Rb}$ atoms. In our coupled-channel calculation of the ground state rovibrational structure, we used the most accurate ground state potentials available from \cite{5}. In section 2, we analyze this structure, and perform a comparison with available high-precision measurements \cite{1, 2}.

Vibrationally cold molecules are preferably made by transferring population from a Feshbach molecular state. For this transfer we selected the pathway that has been proposed by Stwalley \cite{6}, which forms vibrationally cold KRb molecules starting from the highly excited vibrational states using one optical Raman transition and intermediate vibrational levels of the
Figure 1. The ground and excited state potential energy curves of KRb that are used for multi-channel modeling as a function of internuclear separation $R$. Here $a_0$ is the Bohr radius of 0.0529 nm.

3(1) potential. This mechanism was also used to create vibrationally cold RbCs molecules in [7]. Bergeman et al [8] have reported an analysis of perturbations of the vibrational levels of the $2^3\Sigma^+$ potential due to spin–orbit interactions with the neighboring potentials in RbCs.

For the vibrational levels used as intermediate states the 3(1) potential can to first order be described as the nonrelativistic $2^3\Sigma^+$ state. More accurately the strong nonadiabatic interaction with the neighboring 2(1) and 4(1) potentials has to be taken into account. Alternately, we can view this coupling as being due to the spin–orbit interaction between the nonrelativistic $2^3\Sigma^+$, $1^3\Pi$ and $1^1\Pi$ potentials. Therefore in section 3, we perform multi-channel calculations of the rovibrational structure and the vibrationally-averaged transition dipole moments to the ground state levels. The three intermediate excited states that are of interest have $\Omega = 1$ symmetry and are shown in figure 1 together with the ground state potentials of KRb. In addition, panel (a) of figure 1 shows the pathway to form $v = 0\ a^3\Sigma^+$ molecules starting from a gas of Feshbach molecules. Similarly, panel (b) shows the pathway to $v = 0\ \ X^1\Sigma^+$ molecules.

The excited potentials in figure 1 were constructed from RKR data [9, 10] and as well as from our ab initio calculations. The attractive 2(1) potential dissociates to the atomic K(4s) + Rb(5p$^{1/2}$) limit, whereas the two attractive 3(1) and 4(1) potentials dissociate to the K(4s) + Rb(5p$^{3/2}$) limit. At short internuclear separations the potentials can be approximately described by the Hund’s case (a) $n^{2S+1}\Lambda^{\pm}$ symmetry, where $\Lambda$ is the projection of the electron orbital angular momentum along the internuclear axis and $S$ is the total electron spin. In case (a), coupling the electron orbital angular momentum and spin are not mixed. At longer $R$ relativistic effects are important, where the curves can only be described with Hund’s case (c) $m(\Omega = 1)$ labeling.
In section 3, our multi-channel calculation is, however, based on the nonrelativistic excited potentials \(1^1 \Pi, 1^1 \Pi\) and \(2^3 \Sigma\), electronic transition dipole moments to the ground states, and the spin–orbit coupling matrix elements. Some RKR data for the more deeply bound vibrational levels of the \(1^1 \Pi\) and \(2^3 \Sigma\) are available [9, 10]. We extend this information by ab initio electronic structure data and by known long range dispersion coefficients from [11].

The relativistic configuration interaction molecular orbital restricted active space (MOL-RAS-CI) method has been used to calculate potential energy curves, permanent and transition electric dipole moments of the KRb heteronuclear molecule as a function of internuclear separation. We combine this calculation with multi-channel rovibrational structure calculation to obtain Frank–Condon factors between the ground and excited states of KRb.

Finally, in section 4, we describe our calculation of the polarizability of vibrational levels of the \(X^1 \Sigma^+\) and \(a^3 \Sigma^+\) states.

2. Coupled-channel calculation of the ground states

In the Raman transition the initial and final bound vibrational levels belong to the ground \(X^1 \Sigma^+\) and \(a^3 \Sigma^+\) states. In KRb, these states dissociate to the same [Ar]4s(\(^2\)S) + [Kr]5s(\(^2\)S) atomic limit. The two states are coupled via hyperfine interactions: the Fermi-contact and electron and nuclear Zeeman interactions for each of the constituent atoms. For each atom the Fermi-contact interaction couples its electron spin, here \(1/2\), to its nuclear spin. The Zeeman interaction is nonzero since an external magnetic field is used to create Feshbach KRb molecules. The corresponding Hamiltonian for vibrational states in this coupled system has been discussed in [12, 13]. For this paper, we include the effect of the weak magnetic dipole–dipole interaction perturbatively but do not include the effect of the second-order spin–orbit interaction [14].

Numerically solving for eigen pairs of this system is called a coupled-channel calculation. For our calculations we used the electronic potentials of [5]. The atomic masses for \(^{40}\)K and \(^{87}\)Rb are taken from [15], the Fermi-contact term values and electronic \(g\)-factors are from [16] and, finally, the nuclear magnetic moments are from [17]. The nuclear spin of \(^{40}\)K is 4 and that of \(^{87}\)Rb is 3/2.

The vibrational wave functions can be labeled by three nearly conserved angular momentum quantum numbers. These are the relative orbital angular momentum \(\ell\) of the two atoms, its projection \(m_\ell\) along the magnetic field direction, and the projection \(M_F\) of the summed atomic angular momentum \(\vec{F} = \vec{f}_a + \vec{f}_b\) along the same direction. Here, \(\vec{f}_a\) and \(\vec{f}_b\) are total angular momenta of each atom. In fact, we can also write \(\vec{F} = \vec{S} + \vec{I}\), where \(\vec{S}\) and \(\vec{I}\) are the total electron and nuclear spin, respectively.

For our calculations we neglect coupling between states with different \(\ell m_\ell M_F\). In the absence of the magnetic dipole interaction the \(2\ell + 1\) levels with the same \(\ell\) and \(M_F\) quantum numbers are degenerate. For ultracold atoms and molecules we can limit ourselves to \(\ell = 0\) and 2. As the Feshbach molecule created in [2, 18] has \(\ell = 0\) and \(M_F = -7/2\), we will limit ourselves from \(M_F = -11/2\) to \(-3/2\) as in a Raman transition \(M_F\) can change by up to two units depending on the polarization of the light beams.

Figure 2 shows the eigenenergies and properties of eigenfunctions of a coupled-channel calculation with \(M_F = -7/2\) and \(\ell = 0\) at a magnetic field of \(B = 545.9\) G near the dissociation limit. The figure makes evident that mixing between the singlet \(X^1 \Sigma^+\) and triplet \(a^3 \Sigma^+\) states.
Figure 2. Fraction of the $a^3\Sigma^+$ character of the coupled channel eigenstates of the $^{40}$K$^{87}$Rb molecule as a function of their energy at a magnetic field of $B = 545.9$ G. Bound states with $M_F = -7/2$ and $\ell = 0$ are shown. For energy between $-300$ and $-15$ GHz, the levels can be grouped by vibrational quantum number $v$ of the uncoupled $X^1\Sigma^+$ and $a^3\Sigma^+$ potentials with $v = -1$ corresponding to the most weakly bound levels. Panel (a) displays vibrational levels from $v = -4$ to $-9$ and panel (b) is blowup of the near threshold region. Zero energy corresponds to the dissociation energy with both $^{40}$K and $^{87}$Rb in the energetically lowest hyperfine state.

becomes strong within 150 GHz of the limit, where the separation of the vibrational levels in the uncoupled $X$ and $a$ potentials becomes comparable with the hyperfine splitting in the ground states of the two atoms. The vertical axis shows the fraction of the $a^3\Sigma^+$ character in the wave function. A value close to zero (one) corresponds to a state primarily described as a $X^1\Sigma^+$ ($a^3\Sigma^+$) level. Our calculations find nondegenerate hyperfine and Zeeman structure, which are grouped in figure 2 by a vibrational quantum number. Within each group there are twelve sublevels, which for weak mixing corresponds to three singlet and nine triplet sublevels. The vibrational
Figure 3. The hyperfine and Zeeman structure at $B = 545.9$ G of the $\ell = 0$ (black lines) and 2 (red lines) rotational levels of the $v = 0$ vibrational state of the $a^3\Sigma^+$ potential of $^{40}$K$^{87}$Rb. The crosses and triangles indicate the experimentally observed energies from [2]. The theoretical energies have been shifted up by $+15.0$ GHz to coincide with the experimental data. Zero energy corresponds to the dissociation energy of both $^{40}$K and $^{87}$Rb in the energetically lowest hyperfine state. The levels are grouped by the projection quantum number $M_F$. Each $\ell = 2$ hyperfine feature contains three lines, which on the scale of the figure are barely resolved. The splitting is on the order of 0.1 GHz and due to the magnetic spin–spin dipole interaction, which partially lifts the $m_\ell$ degeneracy of the projection quantum number of $\vec{\ell}$.

quantum number is labeled according to the vibrational quantum number of the uncoupled singlet and triplet potential. The $v = -1$ level corresponds to the last uncoupled bound level. The grouping is valid in this case because the two potentials have the same long-range dispersion potential and sufficiently similar scattering lengths that the spacing between vibrational levels of the two potentials is nearly the same in the range of energy shown. For binding energies less than 3 GHz the levels with different vibrational quantum numbers intermix. The level relevant for the experiment of Ni et al [2], which is the initial state of both Raman transitions in figure 1, is the most weakly bound sublevel with $M_F = -7/2$ and has a 0.23 MHz binding energy at $B = 545.9$ G. Here, this state has 80% $a^3\Sigma^+$ character. The weakly bound levels are now fully discussed in [19].

The final states of the Raman transitions are $v = 0$ levels of the $X^1\Sigma^+$ and $a^3\Sigma^+$ potentials. Figure 3 shows the rotational hyperfine and Zeeman structure of the $v = 0$ level of the $a^3\Sigma^+$ potential at $B = 545.9$ G as calculated with the coupled-channel method. The black lines are the $\ell = 0$ bound states and the red lines are the $\ell = 2$ bound state. Notice though that the rotational energy splitting is smaller than that due to the hyperfine and Zeeman interaction. This leads to overlapping spectral features. The hyperfine structure of the two partial waves is nearly identical.
Figure 4. The hyperfine and Zeeman structure of the $v = 0$, $\ell = 0$ level (panel a) and $\ell = 2$ (panel b) of the $X^1\Sigma^+$ state of $^{40}\text{K}^{87}\text{Rb}$ at $B = 545.9$ G. The triangles with one-standard-deviation error bar indicate the experimentally observed energies from [2]. The theoretical energies have been shifted up by $+0.4014$ GHz such that the energetically lowest $\ell = 0, M_F = -7/2$ level coincides with the experimental data. The energy regions shown in the two panels are not the same. Zero energy corresponds to the dissociation energy of both $^{40}\text{K}$ and $^{87}\text{Rb}$ in the energetically lowest hyperfine state. The levels are grouped by the projection quantum number $M_F$.

The main difference is that each $\ell = 2$ hyperfine feature has within it three lines, which are not resolved in the figure. The splitting between these lines is less than 0.3 GHz and is due to the magnetic spin–spin dipole interaction, which partially lifts the $m_\ell$ degeneracy of the projection quantum number of $\vec{\ell}$.

The experiments of [1, 2] have located more than ten sublevels of the $v = 0$ vibrational level of the $a^3\Sigma^+$ potential. We have compared the calculated hyperfine structure of the $v = 0$ level of the triplet state, shifted up by $+15.0$ GHz, with the experimental energies of Ni et al [2], marked by the crosses and triangles in figure 3. The agreement is good.

Figure 4 shows the hyperfine and Zeeman structure of the $v = 0$ vibrational state of the ground $X^1\Sigma^+$ state of $^{40}\text{K}^{87}\text{Rb}$ at $B = 545.9$ G shifted up to $+0.4014$ GHz such that the energetically lowest $\ell = 0, M_F = -7/2$ level coincides with the experimental data indicated by triangles in figure 4. The two panel show energy levels for the lowest two even partial waves. The singlet potential has to first order no hyperfine structure due to the Fermi contact interaction and electronic Zeeman interaction. Hence, the structure in figure 4 is predominantly due to the nuclear Zeeman interaction of both atoms and is on the order of a few megahertz (MHz) at $B = 545.9$ G. In fact, the nuclear Zeeman energy for the $X^1\Sigma^+$ state is given by

$$E_Z = -(g_{I,K}m_K + g_{I,Rb}m_{Rb})\mu_N B,$$  \hspace{1cm} (1)
where $m_K$ and $m_{\text{Rb}}$ are the projections of the nuclear spin of $^{40}\text{K}$ and $^{87}\text{Rb}$ along the magnetic field direction, respectively. We then have $M_F = m_K + m_{\text{Rb}}$. The $g_{r,K}$ and $g_{r,\text{Rb}}$ are nuclear $g$-factors and $\mu_N$ is the nuclear magneton. The $g$-factor of K is about a factor of two smaller than that of Rb. In figure 4, each line can be labeled by $m_K$ and $m_{\text{Rb}}$. The smaller splittings between lines correspond to the levels with different $m_K$ for the same $m_{\text{Rb}}$. The larger gaps between groups of levels correspond to different $m_{\text{Rb}}$. Each line of figure 4, panel (b), contains five unresolved components corresponding to the five $\ell = 2$ sublevels. Unlike the $\ell = 2$ lines of the $a^3 \Sigma^+$ state, the spin–spin dipole interaction here is zero to the first-order and the second-order contribution is very small.

For the $X^1 \Sigma^+$ potential [2] has observed a single hyperfine component for the $\ell = 0$ and 2 rotational states of the $v = 0$ vibrational level. The experiment and theory agree to $\approx 401.4$ MHz in an energy levels. The theoretical energy difference between $\ell = 0$ and 2 components of the $M_F = -7/2$ levels is 6.683 76 GHz, which agrees well with the experimental value of 6.6836(5) GHz given in [2].

### 3. Multi-channel calculation of the excited states

In this section, we model the rovibrational motion of the $^{40}\text{K}^{87}\text{Rb}$ molecule in excited electronic potentials, which are used as intermediates to create vibrationally cold molecules [2]. In particular, we focus on the need to use a multi-channel description of the vibrational structure that includes coupling between the electronic potentials. The origin of coupling can be explained from either the relativistic spin–orbit interaction, which couples nonrelativistic $2S+1 \Lambda \pm$ Born–Oppenheimer (BO) potentials [20] or nonadiabatic mixing of relativistic $\Omega \pm$ potentials. Some of the relativistic potentials as function of internuclear separation $R$ are shown in figure 1. However, in this section we first calculate multi-channel vibrational energies based on the nonrelativistic potentials. We then discuss the effects of the multi–channel calculation on the vibrationally averaged transition dipole moments. Due to the already complex nature of these calculations, we have not included the contributions of hyperfine, Zeeman, or coriolis interactions.

Note that as stated before for a nonrelativistic potential the quantum number $S$, corresponding to the total electron spin $\vec{S}$, and $\Lambda$, corresponding the absolute value of the projection of the total electron orbital angular momentum, is conserved. For a relativistic calculation only $\Omega$, the absolute value of the projection of the summed electronic orbital and spin angular momentum, are conserved. The $\pm$ superscript, only relevant for $\Lambda = 0$ or $\Omega = 0$ states, distinguishing states with opposite reflection symmetries. For a given $\Omega$ symmetry nonrelativistic potentials that satisfy $-S \leq \Omega - \Lambda \leq S$, are coupled by spin–orbit interactions. Strong mixing occurs when the energy splitting between $2S+1 \Lambda \pm$ potentials is on the order of the spin–orbit interaction energy.

In our multi-channel calculation, we use the $X^1 \Sigma^+$ nonrelativistic ground-state BO potential from [5] and the $2^3 \Sigma^+$, $1^1 \Pi$ and $1^3 \Pi$ excited potentials from [21]. All three excited potentials dissociate to the $K(^2S) + \text{Rb}(^2P)$ limit. The previously unknown spin–orbit coupling matrix elements and electronic dipole moments are obtained from our MOL–RAS–CI calculations. Panel (a) in figure 5 shows shows the $R$-dependent spin–orbit matrix elements between the $2^3 \Sigma^+$, $2^1 \Pi$ and $1^3 \Pi$ states. For the spin–orbit interaction between $\Omega = 1$ potentials diagonal matrix elements are zero. As we will be interested in vibrational levels near the bottom of the $3(1)$ potential spin–orbit coupling to $2^1 \Pi$ potential can be neglected. At large $R$ the matrix
Figure 5. (a) the $R$-dependent off-diagonal spin–orbit matrix elements between the $2^3\Sigma^+$ and $1^1\Pi$ potentials (solid line), the $2^3\Sigma^+$ and $1^3\Pi$ potentials (dashed line) and $1^1\Pi$ and $1^3\Pi$ potentials (dash-dotted line). For the spin–orbit interaction between $\Omega = 1$ potentials diagonal matrix elements are zero. Panel b: the $R$-dependent transition dipole moment between the $X^1\Sigma^+$ and two $1^1\Pi$ states. The dipole moments are in units of $ea_0$, where $e$ is the electron charge.

The spin–orbit matrix elements approach $\Delta/3$, where $\Delta$ is the spin–orbit splitting of the $2P$ state of $^{87}$Rb. Panel (b) in figure 5 shows the $R$-dependent transition dipole moment between the $X^1\Sigma^+$ and the $1^1\Pi$ and $2^1\Pi$ states. The dipole moments between the singlet $X^1\Sigma^+$ and the triplet $2^3\Sigma^+$ and $1^3\Pi$ states are strictly zero.

Figure 6 shows the results of a multi-channel calculation of the vibrational levels of the $\Omega = 1$ excited states. We have coupled three channels, $2^3\Sigma^+$, $2^1\Pi$ and $1^3\Pi$, and, in addition, included the rotational potential $\hbar^2J(J + 1)/(2\mu R^2)$ with rotational quantum number $J = \Omega = 1$ to each channel. The vibrational energy on the horizontal axis is relative to the dissociation energy of ground state $^{40}\text{K}$ and $^{87}\text{Rb}$ and thus corresponds to the photon energy for the upward part of the Raman transition. Each vibrational level is represented by three circles, of different
Figure 6. The fraction of $^3\Pi$ (blue), $^3\Sigma^+$ (red) and $^1\Pi$ (green) character of the multi-channel $\Omega = 1$ eigenstates of the $^{40}\text{K}^{87}\text{Rb}$ molecule as a function of energy. The level indicated by the label $v = 23$ corresponds to the $v = 23$ bound state of the $3(1)$ potential used in [2]. Zero energy corresponds to the dissociation energy of both $^{40}\text{K}$ and $^{87}\text{Rb}$ in the energetically lowest hyperfine state. Hence, the energy can be interpreted as the photon energy needed to make upward transition shown in the right panel of figure 1.

The energy range in figure 6 spans from just below the bottom of the $3(1)$ potential (see figure 1) to the atomic $\text{K}(^2\Sigma) + \text{Rb}(^2\text{P}_{3/2})$ limit. The $v = 0$ vibrational level of the $3(1)$ state can be identified at 9200 cm$^{-1}$. For energies $E > 9200$ cm$^{-1}$ levels with a large fraction of $^3\Sigma^+$ character appear. For $E < 9200$ cm$^{-1}$ only the vibrational levels of the $2(1)$ or $^3\Pi$ state exist. Similarly, at $E \approx 10\,900$ cm$^{-1}$ eigenstates with a large fraction in the $^1\Pi$ state appear. This corresponds to the bottom of the $4(1)$ potential. Interestingly, for all eigenstates with energy $E < 10\,900$ cm$^{-1}$ the levels have a small amount, $< 0.01$, of $^1\Pi$ character. The $2(1)$ and $3(1)$ states have a small $^1\Pi$ admixture due to second-order spin–orbit mixing.

In other energy regions, the characterization of levels is less clear. For example, levels with energy larger than $E \approx 10\,200$ cm$^{-1}$ have non-negligible contributions from the $2^3\Sigma^+$ and $1^3\Pi$ states. These BO potentials of [21] cross at this energy and the spin–orbit interaction mixes the two symmetries. The intermediate vibrational level used in [2] and indicated by $v = 23$ in figure 6 is such a mixed state. From our calculation we find that it has a 79% $^3\Sigma^+$, 21% $^3\Pi$ and 0.2% $^1\Pi$ character. The closeness of the $v = 23$ level to the avoided crossing and the theoretical uncertainties in its location make the precise fractions uncertain. In fact, a few hundred cm$^{-1}$ upward shift could potentially remove all $^3\Sigma^+$ and $^3\Pi$ mixing and the $v = 23$ level becomes
Figure 7. Transition dipole moment from the \( v = 0, J = 0 \) \( X^1 \Sigma^+ \) level to the excited \( \Omega = 1 \) levels of the \( ^{40}\text{K}\, ^{87}\text{Rb} \) molecule as a function of the excited-state energy. Zero energy corresponds to the dissociation energy of both \( ^{40}\text{K} \) and \( ^{87}\text{Rb} \) in the energetically lowest hyperfine state. The bound \( v = 23 \) level of the 3(1) potential, used as intermediate state in [2], is marked. The calculated dipole moment to the \( v = 23 \) level is 0.018 au.

A nearly pure \( 2^3 \Sigma^+ \) vibrational level. The \( ^1\Pi \) character, however, is not expected to change significantly.

Figure 7 shows the transition dipole moments between vibrational levels of the multi-channel \( \Omega = 1 \) calculation described above and the \( v = 0, J = \ell = 0 \) rovibrational level of the \( X^1 \Sigma^+ \) potential assuming the electronic dipole moment shown in figure 5. This vibrationally averaged dipole moment describes the downward part of the Raman transition. The energy region is as in figure 6 and the changing character of the excited state vibrational levels is reflected in the transition dipole moments. The start of the vibrational series of the 3(1) and 4(1) potentials are clearly visible in the figure. The vibrational averaged dipole moment from the singlet \( X^1 \Sigma^+ \) state is only nonzero if the multi-channel vibrational levels contains \( ^1\Pi \) character. A larger \( ^1\Pi \) character leads to a larger dipole moment for the downward transition. However, for a nearly pure \( ^1\Pi \) level the dipole moment of the upward transition from the Feshbach molecule, which is mainly triplet in character, will decrease significantly. As a result, efficient Raman transfer depends on the choice of intermediate excited state, which must have favorable overlap with both initial and final states. The intermediate vibrational level used in [2] is again indicated by \( v = 23 \). From our calculation, we find a dipole moment of 0.018 au for the transition from this level. Other vibrational levels both below and above 11 000 cm\(^{-1}\) might be good candidates for Raman transfer. This will require additional investigations.

4. Dynamic polarizability of the ground state vibrational levels

We examine the dynamic polarizability \( \alpha \) of the KRb molecule as a function of laser frequency, \( \omega \), and rovibrational quantum numbers, \( v \) and \( J \), of the uncoupled ground state \( a^3 \Sigma^+ \) and \( X^1 \Sigma^+ \).
potentials. The real part of the dynamic polarizability, among other things, determines the depth of the trapping potential seen by a molecule as

\[ V_0 = -\text{Re}(\alpha(h\omega, v)) \times I, \]  

where \( I \) is the intensity of the laser fields at frequency, \( \omega \). The imaginary part of \( \alpha \) describes the spontaneous or any other decay mechanism that leads to loss of molecules from the trap. Based on its knowledge, laser frequencies can be selected to minimize decoherence effects from loss of molecules due to spontaneous or laser-induced transitions.

The dynamic polarizability of a rovibrational level of the ground state is due to dipole coupling to all other rovibronic and continuum states of the ground and excited potentials. In contrast to the calculations in sections 2 and 3, we do not include multi-channel effects due to either the hyperfine, Zeeman or spin–orbit interaction. Instead, we base the calculation on our relativistic configuration-interaction MOL-RAS-CI determination of adiabatic \( n(\Omega^\pm) \) potentials and relativistic transition dipole moments \( d(R) \) between the ground- and excited states. The relativistic configuration-interaction theory treats the spin–orbit interaction nonpertubatively for the electronic wavefunction. Consequently, we use for the polarizability

\[
\alpha(h\omega, v) = \frac{1}{4\pi\varepsilon_0} \frac{2\pi}{c} \sum_{\Omega' J' M'} |\langle \Omega' v' J' M' | d(R) \hat{R} \cdot \vec{e} | \Omega v J M \rangle|^2 \times \left\{ \frac{1}{E_{\Omega' J'} - i\gamma_{\Omega' v' J'} / 2 - (E_{\Omega v J} + \hbar\omega)} + \frac{1}{E_{\Omega' J'} - i\gamma_{\Omega' v' J'} / 2 + \hbar\omega} - E_{\Omega v J} \right\},
\]

where \( \hat{R} \) is the orientation of the interatomic axis, \( |\Omega v J M \rangle \) and \( |\Omega' v' J' M' \rangle \) are the rovibrational wavefunctions of initial \( \Omega \) and final \( \Omega' \) states, respectively. Here, \( M \) and \( M' \) are the projections of \( J \) and \( J' \) along a laboratory fixed axis. The vector \( \vec{e} \) is the polarization of the laser, \( E_{\Omega v J} \) is the rovibrational energy in the ground \( \Omega \) state and \( E_{\Omega' v' J'} \) is the rovibrational energy of the excited \( \Omega' \) states. Contributions from scattering states or continua of the excited \( \Omega' \) states are also included. The widths \( \gamma_{\Omega' v' J'} \) describe the spontaneous decay rate.

In our calculation of the polarizability dipole transitions to rovibrational levels and continuum of the \( a^3\Sigma^+ \) or \( X^1\Sigma^+ \) potentials as well as those of excited \( 2(0^+/-), 3(0^+/-), 4(0^+/-), 5(0^+/-), 2(1), 3(1), 4(1), 5(1) \) and \( 6(1) \) potentials are included. The \( 0^+ \) states do not contribute to the polarizability of the \( X^1\Sigma^+ \) rovibrational levels.

If a molecule is in a rovibrational level of the ground electronic potential and the frequency of a laser generated optical trap is nearly resonant to some molecular transition, this will lead to transfer of population to the rovibrational level of an excited potential, which then by spontaneous emission can decay to many rovibrational levels of the ground potential. As a result, we lose control over the molecule in the trap. To avoid this we must select trap frequency intervals in which resonant excitation is unlikely. We focus on the dynamic polarizability of the initial and final levels relevant to the Raman transition shown in the right panel of figure 1. Most experimentally used trapping lasers use frequencies that are located in the range between 9000 and 9800 cm\(^{-1}\). In particular, we examine the polarizability at laser wavelengths of 1090, 1064 and 1030 nm.

Figure 8 shows the real and imaginary parts of the polarizability of the last three \( J = 0 \) rovibrational levels (\( v = -1, -2, -3 \)) of the \( a^3\Sigma^+ \) potential as a function of laser frequency. The polarizability has only been evaluated every 0.05 cm\(^{-1}\). Most of the resonances in figure 8 are due to vibrational levels of the \( 3(1) \) potential. The uncertainty in the vibrational level
energies is about 5 cm\(^{-1}\). This estimate is based on a comparison with experimental locations of the vibrational levels starting from \(v = 0\) found in [10]. In the figure, we have assigned the resonances due to transitions from the \(v = -1\) level of the \(a^1\Sigma^+\) potential to even or odd vibrational levels of the 3(1) excited potential. The even \(v\) levels have a stronger dipole moment and thus wider resonance. Away from the resonances the imaginary part of the polarizability is six to seven orders of magnitude smaller than the real part. This indicates that the loss due to spontaneous emission from the excited state is negligible. We also indicate three trap
wavelengths. As we can see from figure 8, the wavelength $\lambda_1 = 1090$ nm, used in the JILA experiments [1, 2, 22], is far away from the resonances and has a very-small decoherence rate. The experimental measurement of the dynamic polarizability of the Feshbach molecule at this wavelength gives $(\alpha / h)^{Feshbach} = 5.7 \times 10^{-5}$ MHz (W cm$^{-2}$)$^{-1}$ [22], whereas our calculation predicts the value of $5.6 \times 10^{-5}$ MHz (W cm$^{-2}$)$^{-1}$ as shown in figure 8. The two other trap wavelengths, $\lambda_2 = 1064$ nm and $\lambda_3 = 1030$ nm, lie around stronger resonances and their loss rate is predicted to be 10–100 times larger.

Figure 9 shows the real part of the polarizability of the $v = 0, J = 0$ level of the $X^1\Sigma^+$ ground state of KRb as a function of laser frequency. Only one resonance is visible. It is due to the lowest rovibrational level of the excited $1^3\Pi(0^+)$ potential. This contribution to the polarizability is due to the spin–orbit mixing with the $2^1\Sigma(0^+)$ potential. The benchmark with the shortest wavelength lies very close to this resonance. However, the precise location of the resonance is unknown. The predicted dynamic polarizabilities at $\lambda = 1090$ and 1064 nm are shown in figure 9. Comparison with the experimentally measured polarizability at 1090 nm [22] gives an uncertainty of our calculation of 13%.

In summary, we performed a spin-coupling treatment that describes the hyperfine and Zeeman structure of the most weakly bound and the most deeply bound vibrational levels of the ground $X^1\Sigma^+$ and $a^3\Sigma^+$ potentials. The agreement with the observed experimental structures [2] is very good. Detailed structural understanding and assignment of the vibrationally cold molecules is key for the coherent control of their interactions. In addition, we used a multi-channel description of the excited vibrational levels that includes $R$-dependent spin–orbit coupling between multiple nonrelativistic $2S+1\Lambda \pm$ potentials. The spin–orbit coupling constants were obtained from an electronic structure calculation. Finally, we examined the dynamic polarizability $\alpha$ of vibrationally cold KRb molecules as a function of laser frequency $\omega$. Based on this knowledge, laser frequencies can be selected to minimize decoherence from loss of molecules due to spontaneous or laser-induced transitions.
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