Ultracold Giant Polyatomic Rydberg Molecules: Coherent Control of Molecular Orientation

Seth T. Rittenhouse* and H. R. Sadeghpour†

ITAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA

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We predict the existence of a class of ultracold giant molecules formed from trapped ultracold Rydberg atoms and polar molecules. The interaction which leads to the formation of such molecules is the anisotropic, long-range charge-dipole interaction. We show that prominent candidate molecules such as deuterated hydroxyl (OD) and KRb should bind to Rydberg rubidium atoms, with energies $E_b \approx 5$–25 GHz at distances $R \approx 0.1$–1 μm. These molecules form in double wells, mimicking chiral molecules, with each well containing a particular dipole orientation. We prepare a set of correlated dressed electron-dipole eigenstates which are used in an on-resonance Raman scheme to coherently control the molecular dipole orientation.

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The ability to tailor and control interactions amongst species in a quantum gas is a primary motivation for topical interface research in atomic, molecular, optical, condensed matter and chemical physics. Ultracold polar molecules and Rydberg atoms share in this distinction for being ideally suited for such studies, as they provide a number of convenient control handles [1–5]. Both polar molecules and Rydberg atoms can have large permanent and induced dipole moments, making them amenable to manipulation with external and optical fields via long-range van der Waals ($R^{-6}$) and anisotropic dipole ($R^{-3}$) forces. Design of synthetic many-body textures and simulations of realistic quantum phases are conditional on this level of control [6,7].

It has been proposed that a Rydberg electron interacting via the zero-range Fermi pseudopotential with a nearby perturbing atom could bind into ultralong range Rydberg molecular states. Isotropic molecules with MHz binding energies, “butterfly” molecules with GHz binding energies and large (tens of debye) permanent dipole moments, and “trilobite” molecules with tens of MHz binding energies and ultralarge (kD) dipole moments [8,9] were predicted to exist in ultracold traps. An experiment with ultracold Rydberg atoms in a dense rubidium magnetooptical trap recently realized the existence of the isotropic ultralong range Rydberg molecules [10].

In this work, we propose the existence of a class of ultralong range macroscopic Rydberg molecules which can be created in ultracold traps. The molecular binding comes courtesy of the interaction of the Rydberg electron with the permanent dipole of the trapped polar molecule. This anisotropic interaction, $\vec{d} \cdot \vec{R}/R^2$, is by far the longest range interaction in the physics of cold neutral atoms and molecules and may open new vistas into the emergent discipline of long-range correlated quantum systems. These giant molecules have deep binding energies, $E_b \approx 20$ GHz, are ultralong range, $R \approx 2000\, \text{a}_0$ [see Fig. 2], and are well protected from the nonadiabatic avoided crossings, which could lead to their premature demise. The double-well structure [left (L) and right (R) wells in Fig. 2], in which the orientation of the polar molecule dipole, $d$, is controlled by the Rydberg electron, resembles the double-well structure which determines the left and right handedness in a chiral molecule, as shown schematically in Fig. 1. We propose a realizable coherent on-resonance Raman scheme to control the orientation of the molecular dipole and prepare dipolar superposition states.

The effective electron-dipole interaction $(a - \frac{1}{2})/R^2$ becomes critical at $a = 0$, resulting from a critical dipole, $d_{cr} = 0.639\, 315$ a.u. [11]. For $a < 0$, the interaction is supercritical ($d > d_{cr}$), and the electron binds to the dipole; for $a > 0$, the dipole is subcritical ($d < d_{cr}$) and the electron does not bind to the dipole. When $d > d_{cr} = 1.63$ D,

![FIG. 1 (color online). A schematic of the two ultralong range Rydberg molecular states which form from the interaction of a Rydberg atom with a polar molecule. The Rydberg electron orbit is exaggerated to highlight the long-range nature of the interactions. The direction of the dipole is from the + to −.](image-url)
electron transfer occurs between the Rydberg atom and the polar molecule [12].

For the discussion outlined here, we treat the molecular dipole to be subcritical, \( d < d_{cr} \), such that degenerate perturbation theory can be employed to obtain the Born-Oppenheimer (BO) potential energy curves. For subcritical dipole moments \( (d < d_{cr}) \), details of the short range electron-molecule physics are unimportant.

The anisotropic electron-dipole interaction potential is

\[
V_{ed}(\vec{R} - \vec{r}) = \frac{\vec{d} \cdot (\vec{R} - \vec{r})}{|\vec{R} - \vec{r}|^3}
\]

where \( \vec{R} \) is the dipole position with respect to the Rydberg core and \( \vec{r} \) is the electron position. If we assume that the dipole is on the \( z \) axis, the matrix elements of this interaction in basis \( |nlm\rangle \) are

\[
\langle nlm|V_{ed}|nl'm'\rangle = \int d^3r \frac{d(Z - r \cos \theta)}{(r^2 + Z^2 - 2rZ \cos \theta)^{3/2}} Y_{lm}^*(\Omega) \times Y_{l'm'}(\Omega) R_{nl}(r) R_{nl'}(r).
\]

With some algebra, the final form for the potential matrix becomes

\[
\langle nlm|V_{ed}|nl'm'\rangle = d \delta_{nm} \sqrt{(2l' + 1)(2l + 1)} (-1)^m 
\times \sum_{l''=|l-l'|}^{l+l'} \left( \begin{array}{ccc} l' & l'' & 0 \\ 0 & 0 & 0 \\ m & -m & 0 \end{array} \right) 
\times \left[ \frac{(l'' + 1)}{Z^{l''+2}} \int_0^Z r^{l''+2} R_{n'l'}(r) R_{nl}(r) dr 
- l'' Z^{l''-1} \int_Z^\infty \frac{1}{r^{l''-1}} R_{n'l'}(r) R_{nl}(r) dr \right].
\]

where \( R_{nl}(r) \) are the Laguerre polynomials and \( (...) \) are \( 3 - j \) symbols, and \( Z = |\vec{R} \cdot \hat{Z}| \). For \( \text{Rb}(nl > 2) \), the quantum defects \( \mu_j \) become progressively negligible—\( \mu_j \sim 0.016 \) produces deviations less than 0.06% in the \( \text{Rb}(n = 35) \) Rydberg spectrum—justifying the use of degenerate perturbation theory.

A molecule becomes “polar”, when the two opposite parity states of the molecule are mixed to create the permanent dipole moment \( d_0 \). The minimum electric field \( E_c \) required to mix these states with a splitting \( \Delta = E_c = \frac{\mu}{\mu_{cr}} \).

Defining the eigenvalues of the potential matrix as \( V^A(R) \), the BO potentials for the interaction of a Rydberg atom with a polar molecule of dipole \( d_0 \) is [13]

\[
V^A(R) = d_0 \left( E_c - \sqrt{\left( E^A_n(R) - \frac{1}{R^2} \right)^2 + F_e^2} \right)
\]

where \( F_e^A(R) = V^A_n(R)/d \) is the electric field at position \( R \) due to the Rydberg electron and \( -\frac{d}{dx} \) is the potential generated by the ion core. This postdiagonalization creates a set of dressed correlated electron-dipole eigenstates, with important implications for the control of the dipolar superposition.

The BO potential curves scaled by the dipole strength \( d_0 \) for \( \text{Rb}(n = 35) \) are shown in Fig. 2 interacting with a \( \Lambda \) doublet molecule with critical electric field \( E_c = 10^{-7} \) a.u. The modulations are due to the Rydberg electron oscillations. The interaction of the ionic core with the dipole, \( \frac{1}{R} \), is seen in the potentials in which the molecular dipole points toward the core. The right panel in Fig. 2 illustrates the transition of the molecular dipole orientation through the avoided crossings. The classification of the dipole moments according to their orientation is evident in this figure. The dashed curves show the evolution of the dipole which points away from the core to that which points toward the core (solid curves). The total molecular symmetry for the polyatomic molecule is either \( \Sigma^+ \) or \( \Sigma^- \), depending on whether the polar molecule is a doublet molecule, as in OD(\( ^3\Pi_{3/2} \)), or a singlet molecule, as in KRB(\( ^1\Sigma_g^- \)).

The formation of the giant Rydberg molecular state is a competitive process between the electron- and core-dipole interactions. Binding occurs when the electronic distribution is sufficiently concentrated, allowing the electron-dipole interaction to overcome the core contribution. The concentration of the electron wave function is in part controlled by the range of \( l \) values available in the degenerate Rydberg manifold: \( l = l_{\text{min}}, \ldots, n - 1 \). If the minimum angular momentum is too large compared to \( n \), the...
The position of the Rydberg core. The presence of a permanent molecular dipole oriented toward or away from the ion core, are shown more clearly in Fig. 4. The two wells support a large amplitude at enormous distances from the right-hand configuration in Fig. 1.

The two outer wells, each corresponding to the molecular dipole oriented toward or away from the ion core, are shown more clearly in Fig. 4. The two wells support a large number of vibrational levels within a typical transition frequency in the 400–500 MHz range. The coupling between the L and R curves is on the order of $O(\frac{\Delta \omega}{\omega})$, which for OD is $\approx 10^{-15}$ a.u. The diagonal corrections to the energies in the $n = 35$ manifold, are, respectively, $3 \times 10^{-9}$ and $10^{-9}$ a.u.

The choice for a realizable polar molecule depends on two factors: such molecules should have subcritical dipoles, but be of sufficient strength for meaningful electron-dipole interaction, and have energy splittings which are a fraction of the Rydberg separation. The hydroxyl radical (OH), a $^2\Pi_{3/2}$, $\Delta \lambda = 1.67$ GHz, was recently magnetically trapped [14] and its cold collision with Xe and He beams were studied [15]. Deuteration of hydrogen radicals reduces the doublet splitting by several factors [13], making them more readily polarizable.

In Table I, we give a list of favorable polar molecules. The ground state of $^{85}$K$^7$Rb has been produced with large phase space density and its dipole moment and rotational splitting ($B_r$) have been established [2]. While the dipole moment for the KRb molecule is small, its small rotational splitting ($2B_r$), and its ubiquity make it a good candidate. The deuterated radical, CD($^2\Pi_{3/2}$), can be polarized with field strength of $F_c \sim 2 \times 10^{-7}$ a.u. and has a large but subcritical dipole moment, 1.46 D [16]. Another potentially realizable candidate is metastable CO($^2\Pi_{1/2}(u = 0)$) which lives for 2.63 ms and its $\Delta \omega$ transition ($\Omega = 1,$...
$J = 1$) is 394.1 MHz and has a dipole moment of 1.38 D [17].

The lowest vibrational levels in $L$ ($0_L$) and $R$ ($0_R$) wells in Fig. 4 can be coherently coupled in a microwave Raman process. This fully on-resonance, but weak intensity two-photon transition, via an intermediate vibrational state ($v_R$) in the extended right well (dashed curve) allows for efficient transfer of population. The configurations in the $L$ and $R$ wells, respectively, are with the molecular dipole pointing toward or away from the ionic core. The coherent Raman scheme ensures that the molecular dipole orientations become entangled. The distance between the dipoles scales roughly as $0.27n^2$, which for $n = 35$ translates to 16.5 nm, allowing large superposition states.

Here, we discuss the coherent control of the dipole orientation in a resonant Raman scheme. Because of the existence of an inner wall in the potential curve which contains the $R$ well, large Franck-Condon factors between $v_R$ and $0_R$ transitions are typically about 0.02. The electronic transition dipole moments, with photons polarized along the internuclear axis, scale as $0.20n^2$; for the $n = 35$ Rydberg state, the electronic transition dipole moment between states in the $L$ and upper $R$ wells has a value of 265.6 a.u., giving a total Raman transition matrix element, $d_{tr} \approx 0.1$ a.u. To preserve the coherence of the superposition states, $|c_\pm| = \sqrt{\frac{1}{2}}[|R| \pm |L|]$, in the presence of the polarization fields, on-resonance microwave field strengths of $F_\mu < F_c$ are desired to not perturb the Rydberg states. This gives a splitting between the two possible superposition states of $\Delta \approx 2\Omega \sim 10^{-8}$ a.u. $\sim 70$ MHz, where $\Omega = d_{tr} \cdot F_\mu$ is the Rabi frequency. This splitting can easily be resolved using current microwave techniques without collapsing the superposition.

In summary, we explore the possibility that giant polyatomic Rydberg molecules could readily form in an ultracold trapped mixture of atoms and molecules, from interaction of Rydberg atoms and polar molecules. These molecules which form in double wells contain dipole configurations which can be coherently controlled in a Raman process. The dipolar interaction of two polarized giant Rydberg molecules could be coupled to the internal superposition states of the polar molecules. Ionization of the Rydberg atom from each $L$ and $R$ well can deterministically measure the orientation of the polar molecule.

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TABLE I. Choice of polar molecules and their properties.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$d_0$ (D)</th>
<th>$\Delta$ (MHz)</th>
<th>$F_c$ (a.u.)</th>
<th>$B_\perp$ (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OD ($^3\Pi_{1/2}$)</td>
<td>1.66</td>
<td>494</td>
<td>$6 \times 10^{-8}$ ~40</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>KRB ($^1\Sigma_g^+$)</td>
<td>0.566</td>
<td>-</td>
<td>$6 \times 10^{-7}$ 0.0371</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>CD ($^3\Pi_{1/2}$)</td>
<td>1.46</td>
<td>897</td>
<td>$1.6 \times 10^{-7}$ ~60</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>CO ($^2\Pi_{1/2}$)</td>
<td>1.38</td>
<td>394</td>
<td>$7 \times 10^{-8}$ 40</td>
<td>[17]</td>
<td></td>
</tr>
</tbody>
</table>

$srittenhouse@cfa.harvard.edu
hsadeghpour@cfa.harvard.edu