Long-Range Molecular Resonances in a Cold Rydberg Gas

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We present evidence for molecular resonances in a cold dense gas of rubidium Rydberg atoms. Single UV photon excitation from the $5s$ ground state to np Rydberg states ($n = 50$–90) reveals resonances at energies corresponding to excited atom pairs $(n - 1)d + ns$. We attribute these normally forbidden transitions to avoided crossings between the long-range molecular potentials of two Rydberg atoms. These strong van der Waals interactions result in avoided crossings at extremely long range, e.g., $\sim 58\,000$ times the Bohr radius (a_0) for $n = 70$.

In most experiments involving ultracold atoms or molecules, the goal is to reach the lowest possible energy state, with respect to both translational and internal degrees of freedom. Ultracold Rydberg gases and plasmas exhibit an interesting contrast: They are systems that are translationally cold, but with significant internal energy [1–5]. Highly excited Rydberg atoms have exaggerated properties [6], including strong long-range interactions and long radiative lifetimes. This unique combination has led to proposals to use ultracold Rydberg atoms for fast quantum gates [7,8]. There have also been proposals [9–13] to form bound molecular states with highly excited atoms, but they have yet to be observed. Here we describe the observation of molecular resonances caused by Rydberg-Rydberg interactions which, while not necessarily corresponding to bound states, have narrow linewidths limited primarily by our laser resolution.

Interactions between highly excited Rydberg atoms scale very rapidly with the principal quantum number n. The principal force between identical atoms, the van der Waals interaction, scales as n^{11} [13], and can easily be the dominant force in a gas of high-n Rydberg atoms. Effects from this coupling were observed more than 20 years ago [14], in the form of line broadening of a dense room-temperature gas, which was attributed to the simultaneous excitation of pairs of closely spaced atoms into strongly interacting Rydberg states. Our experiments exploit the reduced Doppler shifts of an ultracold sample together with a high-resolution laser to provide spectral resolution more than 50 times higher, allowing us to see not only line broadening, but also well-defined molecular resonances. These resonances coincide with the average energy of a pair of states, $(n - 1)d + ns$, both of which are forbidden in single-photon excitation from the $5s$ ground state. We propose that these "pair photoassociation" resonances are due to avoided crossings at long range between molecular potential curves arising from two pairs of Rydberg atoms, $(n - 1)d + ns$ and $np + np$. Near these crossings, the normally dark atomic d and s states mix with the bright p states, and excitation is

allowed. The adiabatic potential curves have flat sections sufficient to produce a sharp peak in the frequency spectrum. Related Rydberg-Rydberg resonances have also been explored in cold collision experiments [4,5], in which Stark tuning facilitates resonant excitation transfer via dipole-dipole interactions.

Theoretical work on long-range molecules involving high-n Rydberg atoms has led to the prediction of two classes of bound molecules, neither of which appears to correspond directly to our observations. In the first [9–12], an atom in the $5s$ ground state is weakly bound within the charge distribution of a Rydberg atom by an attractive interaction with the nearly free Rydberg electron. These states, featuring electronic wave functions of striking spatial complexity, are predicted to have resolvable vibrational levels and large dipole moments. The second class of molecular states involves two nonoverlapping Rydberg atoms [13] interacting exclusively via the long-range dispersion potentials. Interplay between the different terms in these potentials results in shallow potential wells at very large internuclear separations, the so-called "macrodimer" states, for which indirect experimental evidence has very recently been reported [15]. Our observed resonances are caused by the same $np + np$ long-range potential curves described in Ref. [13]. However, they correspond not to minima in the potentials, but instead to avoided crossings between such potential curves.

Our experimental approach has much in common with photoassociative spectroscopy of cold atoms, which has been an essential tool for investigating the long-range molecular potentials associated with low-lying excited atomic states [16,17]. In this technique, two atoms collide in the presence of laser light which is resonant with a transition from the initial continuum ground state to an excited bound state of the molecule. These molecular states are usually excited at large internuclear separations, and are highly vibrationally excited. Our work differs in two respects from most photoassociative spectroscopy: The principal quantum numbers are much

higher, and the molecular resonance is a two-photon excitation, in which both of the interacting atoms are excited simultaneously.

In the experiment, we excite a sample of ultracold ^{85}Rb atoms with pulsed laser light, and subsequently detect them using pulsed field ionization. The ultracold atoms are provided by a vapor-cell magneto-optical trap (MOT) using two diode lasers at 780 nm for trapping and optical repumping. The background pressure is $\sim 10^{-9}$ torr and the MOT loading time is <1 s. The typical peak density of the ultracold sample is 10^{11} cm^{-3} at a temperature of ~ 100 μK. Atoms in the $5s$ ($F = 3$) level are excited to np Rydberg states by intense UV pulses of ~ 7 ns duration. These nearly transform limited pulses (<100 MHz bandwidth) are generated by pulsed (10 Hz) amplification of a tunable, single-frequency, cw ring dye laser beam, followed by frequency doubling in a BBO crystal to $\lambda = 297$ nm. The frequency of the cw (fundamental) laser is calibrated to 20 MHz using saturated absorption in an iodine cell. Laser pulses with energies up to 1 mJ are focused into the MOT cloud, yielding a cylindrical excitation volume ~ 1 mm long and 50–100 μm in diameter. A pair of 95% transparent wire meshes, separated by 2.09 cm, surrounds the cold atom cloud and allows careful nulling of stray fields and extraction of ions produced by pulsed field ionization. The detection sequence is as follows: The trap and repumping lasers are switched off prior to the arrival of the UV pulse (the magnetic field remains on), preventing direct photoionization of atoms excited to the $5p$ level in the trapping process. Approximately 300 ns after the UV interaction, a short (~ 80 ns) high voltage pulse provides a field of ~ 1000 V/cm that ionizes any Rydberg states above $n \sim 28$. The resulting ions are detected by a microchannel plate (MCP).

Laser scans in the vicinity of three different np states are shown in Fig. 1. The molecular resonances are seen as small peaks in the ion signal to the red (low frequency side) of the main np lines. At $n = 70$, typical signals are 3–300 ions per laser shot, depending on MOT and laser conditions. To verify that the frequency offset of the molecular resonance from the atomic np line follows the n^{*-3} scaling of the atomic energy level splittings, we have scaled the frequency axes for the three plots according to $(n^*/60^*)^3$. Here $n^* = n - \delta_p$, and $\delta_p = 2.6415$ is the quantum defect of the $p_{3/2}$ level [18]. Note also that there is significant broadening of the main np atomic resonances. The broadening is predominantly to the red, and increases with laser energy and with n, consistent with attractive Rydberg-Rydberg van der Waals interactions. We observe the molecular resonances over a range of $n = 50$–90.

At large internuclear separations R, the interaction between two atoms, each excited into the same np Rydberg state, takes the form [19,20]
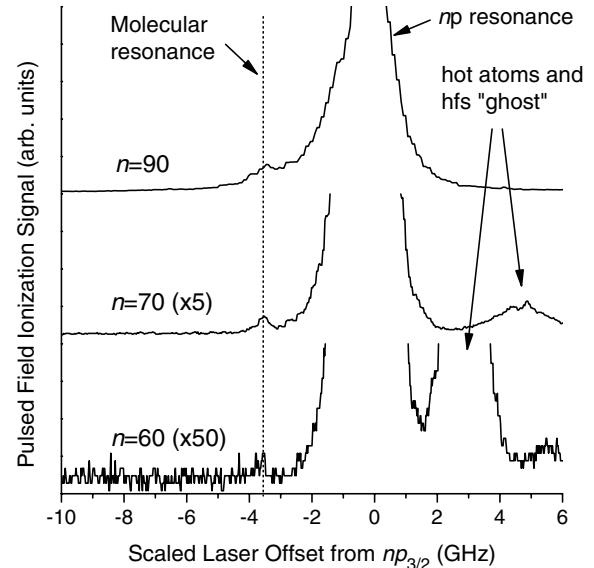
$$V(R) = -C_5/R^5 - C_6/R^6 - C_8/R^8. \qquad (1)$$

FIG. 1. Rydberg spectra near the $60p$, $70p$, and $90p$ transitions, for a peak laser irradiance of ~ 480 MW/cm^2. For $n = 60$, the actual frequency scale is shown; other frequencies are scaled as described in the text. The dashed line corresponds to an offset of 3.56 GHz from $60\,^2P_{3/2}$, 2.20 GHz from $70\,^2P_{3/2}$, and 1.01 GHz from $90\,^2P_{3/2}$. The signal sizes are scaled as indicated: The molecular signal increases by a factor of roughly 30 between $n = 60$ and 90, even though the size of the off-scale atomic peak declines by a factor of at least 15, a lower bound due to saturation at $n = 60$. The peaks at the far right are due to room-temperature background atoms and excitation from $5s$, $F = 2$ due to imperfect optical pumping.

The dispersion coefficients C_5, C_6, and C_8 can be calculated using the expressions of Marinescu [20], and are found to scale with n as $C_5 \sim n^8$, $C_6 \sim n^{11}$, and $C_8 \sim n^{15}$ [13]. The magnitude and sign of these coefficients depend on the molecular symmetry. For the $np + np$ asymptote considered here, there is a total of six pairs of degenerate molecular states with identical coefficients for each pair (see the left-hand side of Fig. 2 for $70p + 70p$). The pair $^1\Sigma_g^+$ and $^3\Sigma_u^+$ has a very large C_6 leading to a strongly attractive potential curve which intersects at long range the curves correlated to the $(n - 1)d + ns$ asymptote. These $(n - 1)d + ns$ potentials also behave according to Eq. (1) [21]. The results for $69d + 70s$ are shown in Fig. 2. These curves are relatively flat in the intersection region, so the crossing occurs at very nearly the asymptotic atomic energy. The experimental spectrum is displayed on the right-hand side of Fig. 2. Beyond alignment of the main np resonance, and division of the left frequency axis by two (since we are comparing a single-photon excitation spectrum with doubly excited potentials), there are no adjustable parameters in this comparison. Within experimental uncertainty, the molecular resonance coincides with the $69d + 70s$ asymptote, in accord with the location of the curve crossing. We note that not only are the $5s \rightarrow (n - 1)d, ns$ transitions dipole forbidden, but there is no atomic state at the energy of the molecular
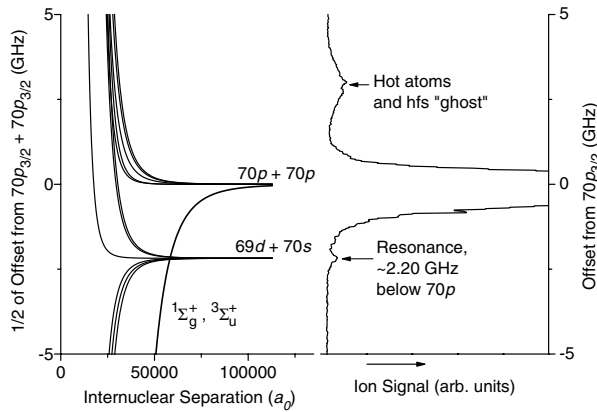
FIG. 2. Left panel: Potential curves between two Rydberg atoms in the vicinity of $n = 70$ (a_0 is the Bohr radius). Right panel: Experimental spectrum; ion signal vs laser frequency. The left frequency axis has been divided by two for the comparison, since the potentials correspond to two excited atoms. The arrows indicate additional features in the spectrum due to incomplete optical pumping in the MOT and the presence of room temperature Rb atoms in the background vapor.

resonance. This energy corresponds, in single-photon excitation, to the *average* energy of the $69d$ and $70s$ states.

An obvious question is why we see a peak in the signal at the energy of the curve crossing. The strongly attractive $np + np$ curve visible in Fig. 2 (labeled $^1\Sigma_g^+$, $^3\Sigma_u^+$) allows excitation of atom pairs whose interaction energy matches the laser detuning from the $np + np$ asymptote. This gives rise to the structureless line broadening to the red of the atomic resonance. In the vicinity of the curve crossing, the $69d + 70s$ and $70p + 70p$ curves are mixed by the dipole couplings between the $70p$ and both $69d$ and $70s$ atomic states, resulting in an avoided crossing not shown in Fig. 2. The dipole coupling strength is on the order of n^4/R^3 atomic units, or $\sim 1.2 \times 10^{-7}$ a.u. (~ 800 MHz) for $n = 70$. In this mixing region, the $69d + 70s$ curve acquires $70p$ character, allowing excitation to it. We have constructed a simple theoretical model for the resulting resonance, which will be described in a future publication. In brief, there is a range $\Delta R \simeq 2400 a_0$ of internuclear separations over which resonance is maintained on the adiabatic potentials, leading to a relatively large number of atom pairs which can be excited, and, hence, a peak in the spectrum. This is an example of the general phenomenon of a spectral peak (often denoted as a satellite) arising from a vanishing derivative of the potential. Our model predicts roughly 750 ions/laser shot for $n = 70$ under the conditions used for Fig. 1, somewhat larger than the observed signal size, but basically in good agreement.

By coincidence, one class of theoretically predicted molecular states with only a single excited electron [11,12] is also predicted to have a resonance in the vicinity of our observed peak. For $n = 70$, the lowest vibrational level is predicted to lie ~ 2 GHz below the np asymptote [22], which is remarkably close to our observed resonance at 2.21(3) GHz. This frequency offset also exhibits the same n^{*-3} scaling as our data. However, additional measurements, discussed below, support our two-excited-atom curve-crossing model, but are inconsistent with these one-excited-atom states. The two-excited-atom macrodimer states [13] cannot explain our observed resonances either, because their potential wells are too shallow.

We have measured the Stark shift of the molecular resonance by applying a uniform electric field during the excitation. Zero field is determined by photoionizing the atoms and minimizing the motion of the ions prior to their extraction. The results, shown in Fig. 3(a), reveal a quadratic Stark shift. This is inconsistent with the predicted linear Stark shift of the one-excited-atom model [11]. For $n = 70$, this long-range molecular state is estimated to have a dipole moment of 1.54×10^3 a.u., or a linear Stark shift of 1.97 GHz in a field of 1 V/cm. This clearly does not agree with our data. Interestingly, the measured shift of the molecular feature is about 40% larger than the average measured shift of the s and d states. We have also measured the dependence of the signal size on the laser irradiance, as shown in Fig. 3(b). A quadratic dependence describes the data well, supporting the two-excited-atom mechanism. The one-excited-atom model calls for a linear irradiance dependence which is not a good fit with the measurements.

In addition to the molecular resonance which coincides with the average energy of $(n - 1)d + ns$ atom pairs, we also see a feature which appears at the average energy of $(n - 1)p + (n + 1)p$. An example in the vicinity of $70p$ is shown in Fig. 4. This peak appears much closer to the main atomic $70p$ resonance than the $69d + 70s$ peak discussed above. The identification of this feature with the $69p + 71p$ atom pair asymptote is consistent with the strongly attractive $^1\Sigma_g^+$ and $^3\Sigma_u^+$ curves from $70p + 70p$ intersecting the relatively flat curves from $69p + 71p$ at
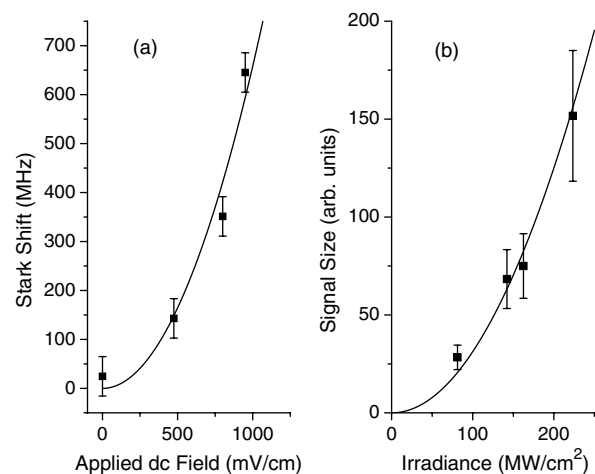

FIG. 3. Stark shift (a) and signal size vs peak laser irradiance (b) of the $n = 70$ molecular resonance. In both cases, the solid curves are quadratic fits to the data.
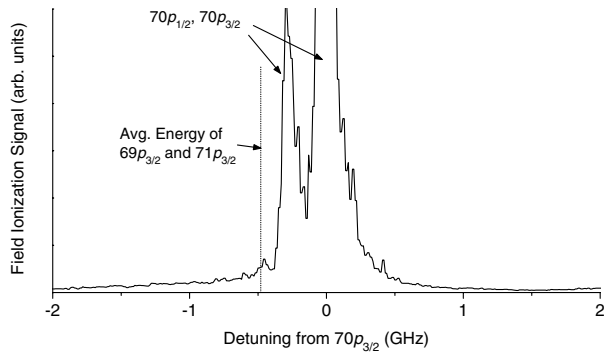
FIG. 4. Spectrum near $70p$ showing a molecular resonance which coincides with the average energy of $69p + 71p$.

very long range, about $75\,000a_0$. Since there is no dipole coupling between np and $(n \pm 1)p$, the interaction responsible for the avoided crossing must be quadrupolar in nature. Based on calculated electronic quadrupole moments, we estimate this coupling to be ~ 0.9 MHz at the crossing. This peak is seen over a range of $n = 50$–70 and its offset from the main np resonance exhibits the characteristic n^{*-3} scaling. We do not expect to see numerous additional peaks for arbitrary combinations of $s + d$ states or $p + p$ states. This is because as the atomic energy differences increase, the dipole and quadrupole matrix elements decrease rapidly. Only those states closest in energy to np contribute significantly, and these are the combinations of states we have observed. We note that the resonance at 2.21 GHz below $70p$ is rather close to both the $69d + 70s$ asymptote at 2.179 GHz and the $68d + 71s$ asymptote at 2.28 GHz. However, the latter has a weaker coupling to $70p + 70p$ by a factor of ~ 2, and should be less important.

In conclusion, we have used high-resolution laser spectroscopy to observe molecular resonances in a cold gas of ^{85}Rb Rydberg atoms. Their locations coincide with the average energy of Rydberg atom pairs. We believe that long-range avoided crossings between two-excited-atom potential curves are responsible for these features. Long-range molecular states involving one Rydberg atom and one ground-state atom are not consistent with our measurements. Our experiment has focused on Rb, but we expect other atoms to also exhibit these resonances. Of course, the details will depend on the quantum defects. We emphasize that the interactions responsible for these resonances take place at very long range, e.g., the curve crossing between $70p + 70p$ and $69d + 70s$ occurs at $58\,000a_0$. This distance can exceed the average nearest-neighbor distance of ground-state atoms, $23\,000a_0$ for a density of 10^{11} cm^{-3}. In this case, the atom pairs responsible for the resonance need not be nearest neighbors, implying that many-body effects should become important. The strong van der Waals interactions responsible for the observed molecular resonances may prove useful in

proposed quantum gates using cold Rydberg atoms [7,8]. In particular, a resonantly excited Rydberg atom can shift a neighboring atom far from resonance, thereby inhibiting its excitation.

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[1] T. C. Killian et al., Phys. Rev. Lett. **83**, 4776 (1999).
[2] S. K. Dutta et al., Phys. Rev. Lett. **86**, 3993, (2001).
[3] M. P. Robinson et al., Phys. Rev. Lett. **85**, 4466 (2000).
[4] I. Mourachko et al., Phys. Rev. Lett. **80**, 253 (1998).
[5] W. R. Anderson, J. R. Veale, and T. F. Gallagher, Phys. Rev. Lett. **80**, 249 (1998).
[6] T. F. Gallagher, Rydberg Atoms (Cambridge University Press, Cambridge, England, 1994).
[7] D. Jaksch et al., Phys. Rev. Lett. **85**, 2208 (2000).
[8] M. D. Lukin et al., Phys. Rev. Lett. **87**, 037901 (2001).
[9] C. H. Greene, A. S. Dickinson, and H. R. Sadeghpour, Phys. Rev. Lett. **85**, 2458 (2000).
[10] B. E. Granger, E. L. Hamilton, and C. H. Greene, Phys. Rev. A **64**, 042508 (2001).
[11] E. L. Hamilton, C. H. Greene, and H. R. Sadeghpour, J. Phys. B **35**, L199 (2002).
[12] M. I. Chibisov, A. A. Khuskivadze, and I. I. Fabrikant, J. Phys. B **35**, L193 (2002); A. A. Khuskivadze, M. I. Chibisov, and I. I. Fabrikant, Phys. Rev. A **66**, 042709 (2002).
[13] C. Boisseau, I. Simboten, and R. Côté, Phys. Rev. Lett. **88**, 133004 (2002).
[14] J. M. Raimond, G. Vitrant, and S. Haroche, J. Phys. B **14**, L655 (1981).
[15] A. L. de Oliveira, M. W. Mancini, V. S. Bagnato, and L. G. Marcassa, Phys. Rev. Lett. **90**, 143002 (2003).
[16] J. Weiner, V. S. Bagnato, S. Zilio, and P. S. Julienne, Rev. Mod. Phys. **71**, 1 (1999).
[17] W. C. Stwalley and H. Wang, J. Mol. Spectrosc. **195**, 236 (1999).
[18] C. J. Lorenzen and K. Niemax, Phys. Scr. **27**, 300 (1983).
[19] A. Dalgarno and W. D. Davison, Adv. At. Mol. Phys. **2**, 1 (1966).
[20] M. Marinescu, Phys. Rev. A **56**, 4764 (1997).
[21] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995); M. Marinescu and H. R. Sadeghpour, Phys. Rev. A **59**, 390 (1999).
[22] C. H. Greene (private communication).