Ultralong Rydberg Cs$_2$ Molecules Investigated by Combined $ab\ initio$ Calculations and Perturbation Theory

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(Dated: May 3, 2014)

Abstract

Vibrational properties of ultralong Rydberg Cs$_2$ molecules are investigated on corresponding potential curves obtained by perturbation theory. The Rydberg Cs$_2$ molecules are associated by a Rydberg Cs($nS$/$nP$) atom ($n = 30 - 70$) and a ground state Cs(6s) atom. The starting point for the perturbation treatment of corresponding Rydberg molecular potential curves is to generate accurate atomic Rydberg states from realistic $ab\ initio$ effective core potential. The calculated results have similar characteristics with available experimental and theoretical investigations on Rydberg Rb$_2$ molecules. And this is the first time that Rydberg molecules are studied at the $ab\ initio$ level.

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I. INTRODUCTION

Owing to the rapid development on ultracold atoms and molecules\cite{1-3}, a novel type of molecules, Rydberg molecules become accessible to nowadays experiments\cite{4, 5}. A Rydberg molecule is typically formed by the unusually long-range interaction between a Rydberg atom and a ground state (or another Rydberg) atom. Consequently Rydberg molecules are classified into two types according to their formation. In the first case, a macrodimer Rydberg molecule\cite{6-9} associated by two Rydberg atoms (A*+B*) has a size larger than 1 $\mu$m and in the second case a butterfly or trilobite like Rydberg molecule\cite{10-13} associated by a Rydberg atom and a ground state one (A*+B) has a typical size of about $10^3 a_0$ (Bohr radius). Since the first calculation of Rydberg molecular potential curves in 2000 by Greene and coworkers\cite{10}, Rydberg molecules have been extensively investigated both theoretically and experimentally\cite{14-17} due to their extraordinary properties such as huge size, large dipole moment, weak bounding energy and long lifetime. In particular, in some fast developing area of quantum physics, Rydberg molecules are more suitable than Rydberg atoms for quantum manipulation with electric field\cite{18, 19}.

The A*+B* and A*+B types of Rydberg molecules have been postulated in Refs. \cite{7} and \cite{10} respectively. Soon experimental evidence\cite{20-22} has been found for the A*+B* type of Rydberg molecules. Later on experimental verification of the A*+B type of Rydberg molecules\cite{14, 23} has been reported. In 2009 both types of Rydberg molecules have been reported to be directly observed experimentally\cite{4, 5}. In Ref. \cite{4} Bendkowsky and coworkers have reported the measured spectra of Rydberg molecular states formed by Rb(5s) and Rb(ns) with high principle quantum number $n = 34, \cdots, 40$. While in Ref. \cite{5} electric field induced Cs Rydberg atom macrodimers bound at internuclear separations of $3 − 9 \mu$m are investigated, focusing on $(63d) + (65d), (64d) + (66d), (65d) + (67d)$ and $(66d) + (68d)$ pairs. Soon after that Rydberg trimers\cite{15} have also been created by a single-step photoassociation. For a better understanding of the mechanism and further manipulations of Rydberg molecules, coherent transfer of initially free pairs of Rb(5s) atoms to Rydberg molecules (Rb*+Rb) have been demonstrated experimentally\cite{24}. Very recently permanent electric dipole moment of a homonuclear Rydberg molecule has been observed\cite{18} to has the order of 1 Debye even for highly symmetric case of Rb(ns)+Rb(5s) which further pave the way for possible experimental manipulation of this type of molecules.

From theoretical point of view, there have been some calculations of the interaction potential curves and vibrational properties of Rydberg molecules\cite{7, 11, 17, 19} most of which focusing on
A*+B* type. The available theoretical calculations have played significant roles in the experimental realization and interpretation of molecular Rydberg states. In Ref. [17] the photoassociation rates of different bound states have been investigated for Rb Rydberg microdimers which implies potential application to quantum information processing. Very recently the electric field control of triatomic Rydberg molecules have been reported [19] which shows their sensitivity to external electric field and non-adiabatic transitions between neighboring Rydberg molecular potential curves. For A*+B type of Rydberg molecules, in general the available theoretical investigations [10, 11] have adopted s wave scattering or perturbation treatment based on Rydberg states from certain empirical electron-core potential for the Rydberg atom. Therefore accurate description of the Rydberg atom is essential for the accuracy of the Rydberg molecular potential curve no matter by scattering or perturbation treatments, in particular when pursuing quantitative agreement with experiments. To meet this challenge, the present work will adopt combined ab initio calculations and a long range analytical form for better description of the electron-core potential of a Rydberg atom to obtain accurate potential energy curves and vibrational properties of a Rydberg molecule. According to our best knowledge this is the first time that Rydberg molecules are studied at the ab initio level.

In this work ultralong Rydberg Cs₂ molecular potential curves dissociating into Cs(nS/nP)+Cs(6s) and corresponding vibrational levels will be investigated (n = 30 – 70). Details of the methods including combined ab initio and analytical description of Cs Rydberg atoms, perturbation treatment of Cs₂ molecular potential curves and diagonalization of Cs₂ vibrational Hamiltonian in Fourier grid discrete variable representation [25] are given in Sections II.A, II.B and II.C respectively. Then the Rydberg Cs₂ molecular potential curves, vibrational levels, equilibrium internuclear distances and ground state binding energies are discussed in Section III. Finally the conclusions of the present work are summarized in Section IV.

II. METHODS

A. Hamiltonian and Wavefunction of Cs Atom

The probability density of Rydberg electron is crucial for the potentials of the long-range Rydberg molecules. Therefore the Rydberg states of a cesium atom need to be accurately solved as a prerequisite for studying Rydberg Cs₂ molecules. Based on central-field approximation, the
cesium atom can be described by a single electron model with the core-electron interaction using an effective core potential. The Hamiltonian of a cesium atom reads

\[ H_{\text{atom}} = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{atom}}(r), \]  

(1)

where \( V_{\text{atom}}(r) \) is the effective core potential. For large \( r \) the effective core potential has standard long range asymptotic behavior as

\[ V_{\text{atom}}(r) = -\frac{e^2}{4\pi\varepsilon_0 r} - \frac{e^2}{(4\pi\varepsilon_0)^2} \cdot \frac{\alpha_c}{2r^4} \]  

(2)

with \( \alpha_c \) being the Cs\(^+\) core polarizability. While for small \( r \) the potential becomes considerably more complicated consequently the short range potentials are directly obtained by \textit{ab initio} calculations using Gaussian09 suite of programs.[26] The CCSD(T) method, coupled cluster including single and double excitations and triple excitations by perturbation, is adopted to get accurate energies. For modern quantum chemistry calculations the CCSD(T) method has been widely used for accurate energy calculations of small molecules[27, 28] due to its balance between speed and accuracy. In this work all \textit{ab initio} energy calculations are performed with Gaussian09 at CCSD(T)/QZVP level of theory and full correlation between all the electrons explicitly involved in the QZVP basis set has been calculated.

Having the Cs atom Hamiltonian at hand, the single electron Schrödinger equation can be solved to get the valence electron wavefunctions. The total wavefunction \( \Psi_{\text{atom}}(r) \) can be separated into the radial and angular parts as \( \Psi_{\text{atom}}(r) = \Psi_{\text{atom}}(r, \theta, \phi) = R_{nl}(r)Y_{m}^{(nl)}(\theta, \phi) \) with \( Y_{m}^{(nl)}(\theta, \phi) \) being the well known spherical harmonics. While the radial wavefunction \( R_{nl}(r) \) can be solved by the numerical methods such as Numerov method[29]. Taking \( X(r) = rR_{nl}(r) \), the radial Schrödinger equation can be written as standard Numerov form \( \frac{d^2X}{dr^2} = -f(r)X \), where \( f(r) = \frac{2m}{\hbar^2} [ E_{nl} - V_{\text{atom}}(r) ] - \frac{l(l+1)}{r^2} \) with the corresponding Cs atom eigenenergy \( E_{nl} \). From the quantum defect theory, the fine structure eigenenergy of Cs atom \( E_{nlj} \) can be obtained with the quantum defects reported in Ref. [30]. With \( E_{nlj} \) it is straightforward to derive the eigenenergy \( E_{nl} \). Discretizing \( r \) by \( r_j = (N - j + 1) \cdot h \), where \( h \) is the step size and \( N \) is the number of total grids, the Numerov integration is written as

\[ X_{i+1} = \frac{\left( 2 - \frac{5h^2}{6} f_i \right) X_i - \left( 1 + \frac{h^2}{12} f_{i-1} \right) X_{i-1}}{1 + \frac{h^2}{12} f_{i+1}} + O(h^6). \]

(3)

The final integration is being done starting from the long range limit where the eigenfunction has asymptotic form \( X_{1.2} = \exp \left( -\sqrt{-2mE_{nl}}r_{1.2}/\hbar \right) \).
B. Perturbation Treatment of Rydberg Cs\textsubscript{2} Molecular Potential Energy Curves

A Rydberg Cs\textsubscript{2} molecule, formed by a ground state Cs(6s) atom and a Rydberg Cs(nl) atom, can be described by a three-body model shown in Fig. \textbf{1}. The A\textsuperscript{+} and e\textsuperscript{−} are the core and the valence electron of the Rydberg Cs(nl) atom respectively and B is the ground state Cs(6s) atom. To be consistent with the above mentioned atomic part, \( r \) is the distance between the valence electron and the Cs\textsuperscript{+} core, while \( r' \) is the distance between the valence electron and the Cs(6s) atom. And the two Cs atoms are separated by a large distance \( R \). The total Hamiltonian can be obtained by taking into account of all the two-body interactions, namely, the molecular Hamiltonian of long-range Rydberg Cs\textsubscript{2} molecule can be written as

\[
H_{\text{mol}} = H_{\text{atom}} + V_{AB}(R) + V_{Be}(r') + T_{AB},
\]

where \( V_{Be} \) (\( V_{AB} \)) is the interaction potential between \( B \) and e\textsuperscript{−} (A\textsuperscript{+} and \( B \))

\[
V_{Be}(r') = -\frac{e^2}{(4\pi\varepsilon_0)^2} \frac{\alpha_a}{2r'^4}
\]

\[
V_{AB}(R) = -\frac{e^2}{(4\pi\varepsilon_0)^2} \frac{\alpha_a}{2R^4}
\]

and \( T_{AB} \) is the kinetic energy of the two Cs atoms. Here \( \alpha_a \) is the polarizability of a ground state Cs(6s) atom and Eqs. (5) is valid for long range interactions. Similar to the atomic effective core potential \( V_{\text{atom}}(r) \), the short range behavior of \( V_{Be}(r') \) is complicated consequently it is directly obtained by \textit{ab initio} calculations. While the short range behavior of \( V_{AB}(R) \) is not needed in the present work since the prime interest of the present work is the long range Rydberg Cs\textsubscript{2} molecules.

Using Born-Oppenheimer approximation, the molecular Schrödinger equation can be separated into two parts and the molecular potential energy curve can be obtained from the electronic Schrödinger equation

\[
(H_{\text{atom}} + V_{Be}(r')) \psi_{el}(r, R) = E_{el}(R) \psi_{el}(r, R)
\]

\[
V_{\text{mol}}(R) = E_{el}(R) + V_{AB}(R)
\]

In this work, the electronic Schrödinger equation Eq. (6a) is solved by perturbation theory. For ultralong Rydberg molecules the interaction potential \( V_{Be}(r') \) has small matrix elements between Rydberg states of \( H_{\text{atom}} \) due to short range characteristics of \( V_{Be}(r') \) and widely delocalized Rydberg electron density, which can also be seen from the results section. Consequently it is valid
to set $H_{atom}$ as zero order Hamiltonian and the interaction potential $V_{Be}$ as perturbation. Since $V_{Be}$ only leads to couplings between the originally non-degenerate atomic states, the corresponding potential curve to the first order perturbation theory reads

$$V_{mol}(R) = V_{AB}(R) + E_{el}(R) = V_{AB}(R) + \langle \Psi_{atom}|V_{Be}(r')|\Psi_{atom}\rangle$$  \hspace{1cm} (7)

Eq. (7) is the potential energy with respect to the corresponding dissociation limit of the two Cs(6s)+Cs(nl) atoms. The final numerical integrations for the perturbation term are calculated by

$$\langle \Psi_{atom}|V_{Be}(r')|\Psi_{atom}\rangle = 2\pi \int \int \int V_{Be}(r') \mathcal{R}_{nl}^2(r) Y_{lm}(\theta, \phi) Y_{lm}^*(\theta, \phi) r^2 \sin \theta dr d\theta d\phi$$

for different $R$ with $r = \sqrt{R^2 + r'^2 - 2Rr'\cos \theta'}$ to properly treat the singular point of the interaction $V_{Be}(r')$ at $r' = 0$ (which behave as $-1/r'$).

C. Numerical Diagonalization of Cs$_2$ Molecular Vibrational Hamiltonian

The vibrational states of Rydberg Cs$_2$ molecules can be obtained by diagonalization of the molecular radial/vibrational Hamiltonian. Having the knowledge of the molecular potential energy $V_{mol}(R)$ the molecular rovibrational Hamiltonian reads

$$H_{mol}^{rovib} = T_{AB} + V_{mol}(R) = \hbar^2 \frac{1}{2\mu} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + V_{mol}(R) + \frac{\hat{J}^2}{2\mu R^2}$$  \hspace{1cm} (8)

with the reduced mass $\mu = \frac{1}{2}m_{Cs}$ and the total angular momentum $\hat{J}^2$. The total rovibrational wavefunction can be written as $\Psi_{mol}(R) = R_{vJ}(R) Y_J^m$ with $R_{vJ}(R)$ being the radial/vibrational wavefunction and $Y_J^m$ the spherical harmonics as mentioned in previous section. The corresponding rovibrational energy level is $E_{vJ}$ with vibrational quantum number $v$ and rotational quantum number $J$. For a given angular momentum $J$, Eq. (8) can be diagonalized to give eigenenergy $E_{vJ}$ and radial/vibrational wavefunction $R_{vJ}(R)$. Numerical diagonalization of Eq. (8) is performed in a Fourier grid discrete variable representation[25, 31] to give vibrational energy $E_{v0}$ and corresponding vibrational wavefunction.
III. RESULTS AND DISCUSSION

A. The Atomic Wavefunctions of Cs\((ns/np)\) Rydberg States

A typical Rydberg electron density is shown in Fig. 2 (for Cs\((30p)\) state as an example). In the inset of Fig. 2 the Cs effective core potential \(V_{\text{atom}}(r)\) is also shown. The effective core potential \(V_{\text{atom}}(r)\) is calculated by Gaussian09 suit of programs for \(r < 50 \, a_0\) with a step size of 0.1 \(a_0\) at CCSD(T)/QZVP level of theory. While for \(r > 50 \, a_0\) the \(V_{\text{atom}}(r)\) is first calculated by Gaussian09 at the same level of theory then fitted to Eq. (2). The fitted core polarizability for Cs\(^{+}\) is \(\alpha_c = -16.0 \, a_0^3\) with a relative fitting error of less than 0.01%. The calculated core polarizability agree well with the experimental value of -15.5443 \(a_0^3\) reported in Ref. [32]. For further calculations the experimental core polarizability \(\alpha_c = -15.5443 \, a_0^3\) is adopted for \(r > 50 \, a_0\). The \textit{ab initio} calculated effective core potential for \(r < 50 \, a_0\) and the analytical one for \(r > 50 \, a_0\) are connected smoothly as shown in the inset of Fig. 2, which generates the full effective core potential \(V_{\text{atom}}(r)\) used for the calculations of atomic wavefunctions.

The \(ns\) and \(np\) states of Cs atom wavefunctions are calculated by numerical integration of Eq. (3) with a step size of 0.1 \(a_0\) and initial condition of the wavefunction at \(r > 2n^2 \, a_0\) which obey asymptotic form \(R_{nl}(r) \propto \frac{1}{r} \exp \left(-\frac{\sqrt{-2mE_{nl}}}{\hbar}r\right)\). As can be seen from Fig. 2 the Rydberg electron density is highly oscillating. The calculated most probable radius for the valence electron of the Cs\((30p)\) state is 1297.7 \(a_0\) which is the typical order of magnitude of the size of a Rydberg atom. For the Cs\((30s)\), Cs\((60s)\) and Cs\((60p)\) states, the calculated most probable radii are 1250.9 \(a_0\), 5989.4 \(a_0\) and 6093.0 \(a_0\), respectively. The size of a Rydberg atom increases rapidly with increasing principle quantum number \(n\) and slightly increases with increasing angular momentum quantum number \(l\), both due to increasing eigenenergy \(E_{nl}\).

B. The Potential Energy Curves of Cs\((ns/np)+\text{Cs}(6s)\) Rydberg Molecules

Having the wavefunctions of Cs atomic Rydberg states at hand, the corresponding Rydberg Cs\(_2\) molecular potentials \(V_{\text{mol}}(R)\) can be obtained according to Eq. (7) with the knowledge of the interaction potentials \(V_{Be}(r')\) and \(V_{AB}(R)\). The long range behaviors of \(V_{Be}(r')\) and \(V_{AB}(R)\) can be well described by the ground state polarizability \(\alpha_a\) of Cs atom according to Eq. (5). The Cs atom polarizability \(\alpha_a\) has been obtained in the same way as the above mentioned core polarizability \(\alpha_c\), namely, by fitting of the \textit{ab initio} interaction energy \(V_{Be}(r')\) of \(r' > 50 \, a_0\) calculated by Gaussian09.
suit of programs at CCSD(T)/QZVP level of theory. The fitted ground state cesium atom polarizability is $\alpha_a = -416.3 \ a_0^3$ with a relative fitting error of less than 0.002%. The atom polarizability $\alpha_a$ is significantly larger than the core polarizability $\alpha_c$ since the outmost 6$s$ valence electron of the Cs atom can be easily polarized. For $r' < 50 \ a_0$, $V_{Be}(r')$ has been calculated by Gaussian09 suit of programs at CCSD(T)/QZVP level of theory with a step size of 0.1 $a_0$.

The calculated potential energy curves of Rydberg Cs$_2$ molecules are shown in Fig.5 for Cs(30s/30p)+Cs(6s) and Fig.4 for Cs(60s/60p)+Cs(6s). The potential curves also oscillate due to the oscillating characteristics of the atomic Rydberg electron density. For details, the potential curves dissociating into 6$s$ ground state and $ns \ (np)$ Rydberg state are shown in the upper (bottom) panels of Fig.5 and Fig.4. Due to increasing size of a Rydberg atom with angular momentum quantum number $l$, each bottom panel ($np+6s$) has a larger equilibrium internuclear distance for the outmost potential well than that of the upper panel ($ns+6s$). In general the Rydberg molecules can be associated to the outmost potential well more efficiently than other potential wells. As far as the outmost potential well is concerned, the dissociation energy $D_e$ of the bottom panel ($np+6s$) is found to be considerably larger than the upper panel ($ns+6s$) which reflects stronger interaction between $np$ and 6$s$ states than the one between $ns$ and 6$s$ states for a given principle quantum number $n$. The calculated results for Cs*+Cs agree with the reported trends for Rb*+Rb in Ref. [10].

Details of the dissociation energies $D_e$ and equilibrium internuclear distance $R_{min}$ for the outmost potential wells of Rydberg Cs$_2$ molecules associated from different atomic states are shown in Table I. Following the same symbols adopted throughout the present work, a Rydberg Cs$_2$ molecule is formed starting from a ground state Cs (6$s$) atom and a Rydberg state Cs ($nl$) atom. Detailed investigations are performed for the principle quantum number $n$ varying from 30 to 70. As can be seen, the dissociation energy $D_e$ decreases almost in an exponential way with increasing principle quantum number $n$ of the Rydberg atom which agrees with the experimentally observed trends for Rb*+Rb in Ref. [4]. This is because the Rydberg electron density becomes more delocalized as the principle quantum number $n$ becomes larger. As a result the outmost maximum of the electron density, namely the most probable radial probability, decreases with increasing $n$ which weakens the interaction between the two Cs atoms. While the molecular size, which is reflected by $R_{min}$ for the outmost potential well, increases according to the well known $n^2$ rule. By fitting the data reported in Table I one finds the relations $R_{min} = 1.65n^2$ for $ns+6s$ Rydberg Cs$_2$ molecules and $R_{min} = 1.68n^2$ for $np+6s$ ones, which are quite close to each other.
C. Vibrational States of Cs\((ns/np)+\text{Cs}(6s)\) Rydberg molecules

To further understand properties of the ultralong Rydberg Cs\(_2\) molecules, the molecular vibrational energy levels and wave functions are calculated based on the above mentioned potential energy curves. As mentioned in the method section, numerical diagonalization of Eq. (8) is performed in a Fourier grid discrete variable representation\(^{[25]}\) to give vibrational energy \(E_{\nu 0}\) and corresponding vibrational wavefunction. Table II shows some vibrational energies \(E_{\nu 0}\) of the Rydberg Cs\(_2\) molecule dissociating into Cs\((30s)\) and Cs\((6s)\) states. A total of 15925 grids equally spaced from \(R=107.5\ a_0\) to \(R=1699.9\ a_0\) with a step of 0.1 \(a_0\), which covers 17 potential wells, are adopted for numerical diagonalization. The diagonalization finds 58 vibrational bound states among which 10 states are predominately located in the outmost potential well. Also shown in Table II are the average internuclear distance \(\langle R \rangle\) and variance \(\langle \Delta R \rangle = \sqrt{\langle (R - \langle R \rangle)^2 \rangle}\) of each corresponding vibrational state. In general the Rydberg molecules can be associated to the outmost potential well more efficiently than other potential wells. Therefore Table II shows all the vibrational states which are predominately located in the outmost potential well. In this work all the vibrational energies are reported with respect to the corresponding dissociation energy. As can be seen the most deeply bound state in the outmost potential well is located at -498.5 MHz with an average internuclear distance \(\langle R \rangle\) of 1246.6 \(a_0\). Compared to the corresponding \(D_e = -538.2\) MHz a relatively large zero point energy of about 40 MHz is found and the equilibrium vibrational frequency in this potential well is about 78 MHz according to the corresponding fundamental excitation energy.

Similar calculations have been done for the Rydberg Cs\(_2\) molecules dissociating into Cs\((30p)\) and Cs\((6s)\) states. A total of 15251 grids equally spaced from \(R=174.8\ a_0\) to \(R=1699.8\ a_0\) with a step of 0.1 \(a_0\), which covers 15 potential wells, are adopted for numerical diagonalization. In total 80 vibrational bound states are found among which 17 ones are predominately located in the outmost potential well. Table III shows all the 17 vibrational states in the outmost potential well. The most deeply bound vibrational states are found to be located at -1391.0 MHz with average internuclear distance \(\langle R \rangle\) of 1292.5 \(a_0\). Compared to the corresponding \(D_e = -1455.9\) MHz the zero point energy is about 65 MHz and the equilibrium vibrational frequency in this potential well is about 128 MHz according to the corresponding fundamental excitation energy.

In general, as the vibrational energy level increases the mean distance \(\langle R \rangle\) and variance \(\langle \Delta R \rangle\) increase due to approaching of the dissociation limit as can be seen in Tables II and III. How-
ever, for the highest few vibrational states in Tables II and III they already have considerable population in the inner potential wells leading to quite large variances $\langle \Delta R \rangle$ and decrease of the mean distances $\langle R \rangle$. Comparison between the above mentioned vibrational energies and the ones obtained from diagonalization of a relatively smaller Hamiltonian matrix which only covers the outmost potential well reveals that the vibrational levels in the outmost potential well can also be accurately obtained by the latter calculation (diagonalizing a smaller matrix). The root means square deviations between this two calculations are found to be less than 0.02 MHz for both the lowest 7 states in Table II and the lowest 12 states in Table III. If only the well bounded (lowest few) states are considered the deviations between the above mentioned two calculations are almost zero. To check the convergence of the above calculations, the vibrational energies in Tables II and III are further compared with results from diagonalization of a larger Hamiltonian matrix which covers the long range limit up to $R = 4000 \, a_0$. The root mean square deviations between the two calculations are about 0.03 MHz for the vibrational energies in Table III and 0.1 MHz for the ones in Table III. Again the deviations are almost zero if only the well bounded (lowest few) states are considered.

Based on the above mentioned error analysis, further investigations on vibrational states of Rydberg Cs$_2$ molecules dissociating into Cs(6s) and Cs(nl) with high principle quantum number $n$ are performed by covering only the outmost potential well. For the Cs(60s/60p)+Cs(6s) molecules 13583/12587 grids equally spaced from $R=5641.7/5741.3 \, a_0$ to $R=6999.9 \, a_0$ with a step of 0.1 $a_0$ are adopted. Table IV shows 3 vibrational bound states in the outmost well for Cs(60s)+Cs(6s) case and 5 vibrational bound states in the outmost well for Cs(60p)+Cs(6s) case. The corresponding zero point energy and equilibrium vibrational frequency in the outmost potential well of Cs(60s/60p)+Cs(6s) are 1.5/2.6 MHz and 2.7/4.9 MHz, respectively.

IV. CONCLUSIONS

Ultralong range Rydberg molecules have been extensively studied in the past decade due to its unique properties such as huge size, large dipole moment and long lifetime. In the present work ultralong Rydberg Cs$_2$ molecules formed by Cs($ns$/np)+Cs(6s) for $(n = 30 \, - \, 70)$ have been investigated focusing on molecular potential curves and vibrational properties. The Rydberg molecular potential curves are calculated by perturbation theory based on accurate Rydberg atom wavefunctions. The Rydberg atom wavefunctions are generated from realistic ab initio effective core
potential rather than some empirical effective core potential, which serves as a good starting point for further calculations of potential energy curves. The calculated potential energy curves have oscillating nature due to the oscillation of the Rydberg electron density. The investigated Rydberg Cs$_2$ molecular size increases with $n$ according to $R_{\text{min}} = 1.65n^2$ for Cs($ns$)+Cs($6s$) case and $R_{\text{min}} = 1.68n^2$ for Cs($np$)+Cs($6s$) case. The dissociation energy of the outmost potential well decreases almost exponentially with increasing principle quantum number $n$ but increases dramatically with increasing angular momentum quantum number $l$. The largest binding energy of the vibrational ground states studied in this work is 1391.0 MHz for Cs($30p$)+Cs($6s$) case and quickly decreases to a few MHz for $n = 70$ case. According to our best knowledge this is the first time that vibrational properties of Cs$^*$+Cs have been investigated quantitatively at the ab initio level. Consequently the reported results are expected to play important roles for future experiments on observation and manipulation of Cs$^*$+Cs kind of molecules. For each vibrational levels predominantly located in the outmost potential well, apart from the vibrational energies, the mean values and variances of the internuclear distances are also reported which may provide further clues for the experimentalists.

**Acknowledgments**

This work was supported in part by 973 Program of China under Grant No. 2012CB921603, the National Natural Science Foundation of China under Grant No. 11004125, International science & technology cooperation program of China (2011DFA12490), National Natural Science Foundation of China under Grant Nos. 10934004, 60978018, 11274209 and NSFC Project for Excellent Research Team (61121064).
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Figure Legends

Fig. 1

Rydberg molecule structure and coordinate system. The $A^+$ and $e^-$ are the core and the valence electron of the Rydberg Cs($nl$) atom respectively and $B$ is the ground state Cs(6$s$) atom. See the text for details.

Fig. 2

The radial probability density $\rho(r) = |rR_{nl}|^2$ of Cs(30$p$) atom. The effective core potential $V_{\text{atom}}(r)$ of the Cs atom is shown in the inset.

Fig. 3

Molecular potential curves for Cs(30$s$)+Cs(6$s$) (Upper) and Cs(30$p$)+Cs(6$s$) (Bottom).

Fig. 4

Molecular potential curves for Cs(60$s$)+Cs(6$s$) (Upper) and Cs(60$p$)+Cs(6$s$) (Bottom).
TABLE I: The calculated dissociation energy $D_e$ and equilibrium internuclear distance $R_{min}$ for the outmost potential well of a Rydberg Cs$_2$ molecules associated from a Rydberg Cs($ns/np$) atom and a ground state Cs(6s) atom.

| $n$ | $R_{min}$ ($a_0$) | $D_e$ (MHz) | $R_{min}$ ($a_0$) | $D_e$ (MHz) |
|-----|------------------|-------------|------------------|-------------|
| 30  | 1244.6           | -538.2      | 1291.4           | -1455.9     |
| 35  | 1787.0           | -197.3      | 1843.2           | -542.7      |
| 40  | 2427.9           | -84.1       | 2493.5           | -234.0      |
| 45  | 3167.4           | -40.0       | 3242.5           | -112.5      |
| 50  | 4005.7           | -20.8       | 4090.2           | -58.8       |
| 55  | 4942.7           | -11.5       | 5036.8           | -32.8       |
| 60  | 5978.6           | -6.8        | 6082.2           | -19.3       |
| 65  | 7113.5           | -4.2        | 7226.5           | -11.9       |
| 70  | 8347.2           | -2.7        | 8469.8           | -7.6        |
TABLE II: Vibrational properties of Cs(30s)+Cs(6s) Rydberg molecules. $E_{\nu 0}$, $\langle R \rangle$ and $\langle \Delta R \rangle$ are the vibrational energy, mean value and variance of the internuclear distance $R$, respectively.

| $E_{\nu 0}$ (MHz) | -498.5 | -420.5 | -347.4 | -279.6 | -217.3 | -160.9 | -111.2 | -69.2 | -32.7 | -10.1 |
|-------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| $\langle R \rangle$ ($a_0$) | 1246.6 | 1250.8 | 1255.8 | 1261.5 | 1268.4 | 1276.6 | 1286.5 | 1285.9 | 1258.1 | 1328.0 |
| $\langle \Delta R \rangle$ ($a_0$) | 18.6 | 32.9 | 43.8 | 53.6 | 63.3 | 73.4 | 85.3 | 122.0 | 215.5 | 218.4 |
TABLE III: Vibrational properties of Cs(30p)+Cs(6s) Rydberg molecules. $E_{\nu 0}$, $\langle R \rangle$ and $\langle \Delta R \rangle$ are the vibrational energy, mean value and variance of the internuclear distance $R$, respectively.

| $E_{\nu 0}$ (MHz) | -1391.0 | -1262.7 | -1138.9 | -1019.8 | -905.5 | -796.2 | -692.1 | -593.4 | -500.4 |
|-------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| $\langle R \rangle$ ($a_0$) | 1292.5  | 1295.0  | 1297.7  | 1300.6  | 1303.8  | 1307.3  | 1311.1  | 1315.5  | 1320.4  |
| $\langle \Delta R \rangle$ ($a_0$) | 14.5    | 25.5    | 33.4    | 40.2    | 46.5    | 52.4    | 58.3    | 64.1    | 70.1    |
| $E_{\nu 0}$ (MHz) | -413.2  | -332.4  | -258.3  | -191.8  | -132.8  | -86.1   | -38.5   | -8.9    |         |
| $\langle R \rangle$ ($a_0$) | 1325.9  | 1332.3  | 1339.2  | 1345.3  | 1351.0  | 1256.0  | 1268.8  | 1247.9  |         |
| $\langle \Delta R \rangle$ ($a_0$) | 76.2    | 82.8    | 91.7    | 101.3   | 120.4   | 225.3   | 299.4   | 377.1   |         |
TABLE IV: Vibrational properties of Cs(60s)+Cs(6s) and Cs(60p)+Cs(6s) Rydberg molecules. $E_{v0}$, $\langle R \rangle$ and $\langle \Delta R \rangle$ are the vibrational energy, mean value and variance of the internuclear distance $R$, respectively.

|       | $60s + 6s$       |       | $60p + 6s$       |       |       |       |
|-------|-----------------|-------|-----------------|-------|-------|-------|
| $E_{v0}$ (MHz) | -5.3 | -2.6 | -0.7 | $E_{v0}$ (MHz) | -16.7 | -11.8 | -7.5 | -4.0 | -1.3 |
| $\langle R \rangle$ ($a_0$) | 5995.5 | 5930.9 | 6076.7 | $\langle R \rangle$ ($a_0$) | 6092.2 | 6116.9 | 6149.9 | 6167.6 | 6076.6 |
| $\langle \Delta R \rangle$ ($a_0$) | 100.3 | 352.6 | 457.4 | $\langle \Delta R \rangle$ ($a_0$) | 74.0 | 133.7 | 185.6 | 272.2 | 552.8 |
FIG. 1: Liu et al
FIG. 2: Liu et al
FIG. 3: Liu et al
FIG. 4: Liu et al