Formation of ultracold Cs$_2$ molecules through the double-minimum Cs$_2$ 3 $^1\Sigma_u^+$ state

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We present a simple model of ultracold cesium dimer formation in which the photoassociation into rovibrational levels of the double-minimum Cs$_2$ 3 $^1\Sigma_u^+$ state above its internal barrier enables spontaneous or stimulated emission into the lowest rovibrational levels of the Cs$_2$ 1(X) $^1\Sigma_g^+$ ground electronic state. The transition dipole moment should be sufficiently large for observation of such spectral transitions. The use of the Cs$_2$ 3 $^1\Sigma_u^+$ double-minimum potential could be extended to molecular Bose-Einstein condensates in which an optical trap can be employed for trapping of both atomic and molecular species.

I. INTRODUCTION

Recent advances in ultracold cooling and trapping of molecules have greatly stimulated an interest in developing the most feasible method for obtaining a molecular quantum gas. Efforts have been concentrated on finding ways to produce ultracold molecules, which cannot be easily cooled by the two level atomic schemes [1–6].

A two-photon Raman pumping process, e.g., stimulated Raman adiabatic passage, should be more effective for producing ground-state ultracold molecules than one- or two-step photoassociation followed by spontaneous emission. Applying the two-photon Raman process, one can drive the free atoms into bound molecules in a controlled manner, such that the molecules are not formed in a statistical mixture of rovibrational states, but rather in one of the lowest well defined rovibrational states. This may eventually lead to formation of internally ultracold molecules. More recently, ultracold molecules have been produced through stimulated Raman photoassociation [7] to the lowest triplet state of Cs$_2$, with comparable efficiencies to one-photon photoassociation followed by spontaneous emission (stabilization). The same process has been applied to even colder samples of Rb [8] and ^{7}Li [9] Bose-Einstein condensates, although ultracold molecules (or a molecular Bose-Einstein condensate) have not been directly detected.

Double-minimum states in alkali dimers are always interesting since they offer the observation of intriguing spectroscopic quantum interference patterns from the two Condon points located within the outer potential well [10,11]. In connection with ultracold cesium atom collisions, it would be of considerable interest to investigate a photoassociation excitation process into the outer potential well. Of special significance is the photoassociation into the vibrational-rotational levels that lie above or just below the potential barrier that divides the two potential wells. Levels just above

the barrier can spontaneously radiate at the inner turning point at short internuclear distances and thus, by downward vertical transition, end up at the very bottom of the Cs$_2$ 1(X) $^1\Sigma_g^+$ ground state. The levels just below the barrier could tunnel into the inner potential well and also reach the inner turning point. Such a photoassociated molecule could be translationally ultracold with an average kinetic energy similar to that of the free atoms (typically 100 μK for Cs) in a magneto-optical trap (MOT). Tunneling through a potential barrier in the case of the Cs$_2$ 0_g^- pure long-range state has been recently discussed in order to explain ''giant'' structures in the Cs$_2^+$ ion signal of the Fioretti *et al.* experiment [12–14]. Photoassociation into the outer potential well below the barrier forms a special type of molecule with very large amplitude vibrations. It is assumed that a molecule in such an elongated state may become very reactive. For example, one could imagine the reaction of such a molecule with H$_2$ resulting in two CsH molecules, with a large reaction rate coefficient.

We present here a process for forming ultracold ground-state molecules in their lowest rovibrational states, with long-term stability. Our approach shows an efficient and simple way for making both externally and internally ultracold molecules. If trapped (optically or magnetically), these molecules present an excellent sample for further studies, e.g., toward producing a quantum degenerate molecular system.

II. RESULTS

The simple two-photon process, which renders possible the formation of a large number of ultracold Cs$_2$ molecules in their lowest rovibrational levels of the ground state, is presented in Fig. 1. Potential curves have been taken from the *ab initio* calculations of Spies and Meyer [15]. In order to be successful, this process should have an appreciable transition dipole moment for both spectral transitions in question. Since there are no complete calculations of the relevant transition probabilities in the case of the cesium dimer, we adopted a theoretical transition dipole moment function $D(R)$ for this transition available from Li$_2$ *ab initio* calcula-

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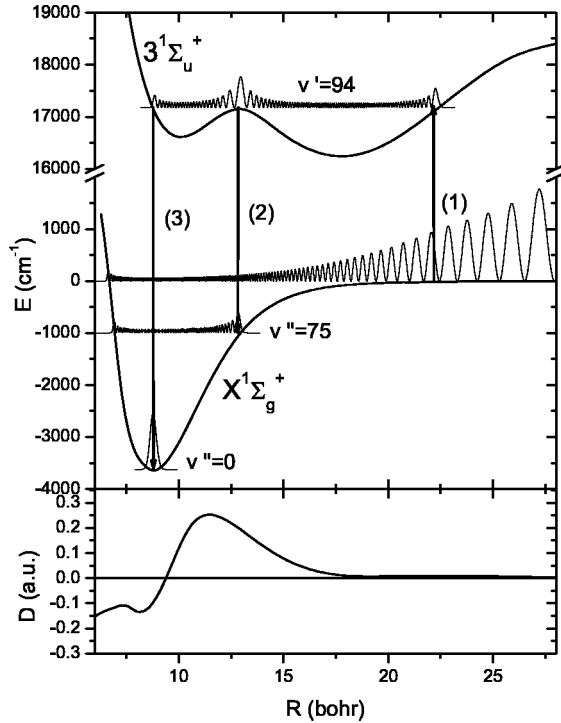†Electronic address: w.stwalley@uconn.edu

FIG. 1. Potential curves of the ground and double-minimum states with corresponding wave functions and radiative transitions: (1) the photoassociation transition from the ground free to the bound $3\,^1\Sigma_u^+$ state, (2) the $3\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ transition at the barrier dividing the two wells, and (3) the $3\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ transition at the inner wall of the $3\,^1\Sigma_u^+$ potential. The lower panel shows the transition dipole moment as a function of the internuclear distance based on scaling from the analogous transition in Li_2 to the Cs_2 dimer.

tions [16]. In the latter case, the $2\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ transition in Li_2 is an analogous transition to $3\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ transition in Cs_2. $D(R)$ describes behavior of the transition dipole moment as a function of R from the ground state to the double-minimum potential. However, the internuclear distance R is scaled by the factor of 1.483, which is the ratio of the Cs_2 $3\,^1\Sigma_u^+$ outer well equilibrium distance R_e^{ou} of the outer well to the R_e^{ou} of the corresponding Li_2 $2\,^1\Sigma_u^+$ outer well potential. The absolute value of the $D(R)$ function was adjusted in order to match the absorption coefficient of the measured Cs_2 611.5 nm absorption profile of the corresponding diffuse band [17]. This diffuse band was usually observed in a high-resolution emission experiment with single longitudinal mode laser excitation [10]. The relevant fluorescence spectrum revealed an exquisite interference pattern. This interference continuum exhibited fine and coarse interference undulations due to the two Condon points. This structured continuum is completely washed out in absorption or emission experiments at elevated temperatures.

In order to describe the process of ultracold molecule formation, the squares of the wave function relevant for the photoassociative process are shown in Fig. 1. From the ultracold free state described by the s-wave function $\phi(E)$ that scatters within the ground $X\,^1\Sigma_g^+$ state (energy of the free state corresponds to the average relative kinetic energy of the

collision of 100 μK), the absorption of a photon Eq. (1) produces excitation into the bound vibrational state v of the excited $3\,^1\Sigma_u^+$ electronic state. This transition occurs at large interatomic distances $R \approx 22$ bohrs in the region of the outer turning point of the excited vibrational state. Vibrational wave functions for bound states v' above the barrier of the $3\,^1\Sigma_u^+$ state have considerable amplitude at both turning points and in the vicinity of the barrier. By spontaneous photon emission in the region of the barrier, $R \approx 12$ bohrs [$3\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$, transition (2)], the bound vibrational states v'' of the ground electronic state $X\,^1\Sigma_g^+$ are produced in relatively high vibrational quantum numbers. In contrast, for transitions around the inner turning point at $R \approx 7-8$ bohrs (3), it is possible to populate the lowest vibrational states $v''(X\,^1\Sigma_g^+)$.

The wave functions in Fig. 1 have been calculated by using the mapped Fourier Grid Hamiltonian method. The range of internuclear separations from 5.5 bohrs up to 600 bohrs is divided into 928 grid points [18]. Using such precise division, we calculated all necessary wave functions and vibrational energies in these two electronic states, with rotational quantum number $J=0$. We found that $v'=88$ and 89 levels from the outer potential well of the $3\,^1\Sigma_u^+$ state tunnel into the inner well. The next $v'=90$ level lies just above the barrier. For the ultracold free state the s-wave function was calculated by means of the four-point Runge-Kutta method. For calculation of the excitation and emission Franck-Condon factors we used the same grid division for both states involved in the radiative transition processes.

The probability of photoassociation, $P_{PA}(E,v')$, from the free $\phi(E)$ state into the bound $v'(3\,^1\Sigma_u^+)$ state, is proportional to the square of the modulus of the matrix element for the electronic transition dipole moment $D(R)$ for this transition,

$$P_{PA}(E,v') \propto |\langle v'(3\,^1\Sigma_u^+)|D(R)|\phi(E)\rangle|^2. \qquad (1)$$

In Fig. 2 we present the probability of photoassociation from the ultracold free state into the double-minimum potential $P_{PA}(E,v')$ which is dependent on the energy difference between the initial and final states, ΔE involved in transition, i.e., on the wavelength of the photoassociation laser λ_{PA}. The values have been normalized to unity by dividing them by the maximum value, which approximately corresponds to the minimum in the relevant difference potential. Thus, although the largest probability of excitation is into the lowest vibrational states, localized within the outer minimum of the double-minimum potential curve, the probability of excitation of vibrational states above the barrier is not negligible. The arrow in Fig. 2 shows the wavelength at which $v'=94$ is excited ($\lambda_{air}=581.75$ nm).

The transition probability for the spontaneous emission $P_{SE}(v',v'')$ from different vibrational levels of the double minimum $3\,^1\Sigma_u^+$ potential to different vibrational levels of the ground $X\,^1\Sigma_g^+$ state is presented in Fig. 3. As in the case of probability for photoassociation, the probability of spontaneous emission is here also proportional to the square of the modulus of the matrix element of the electronic transition
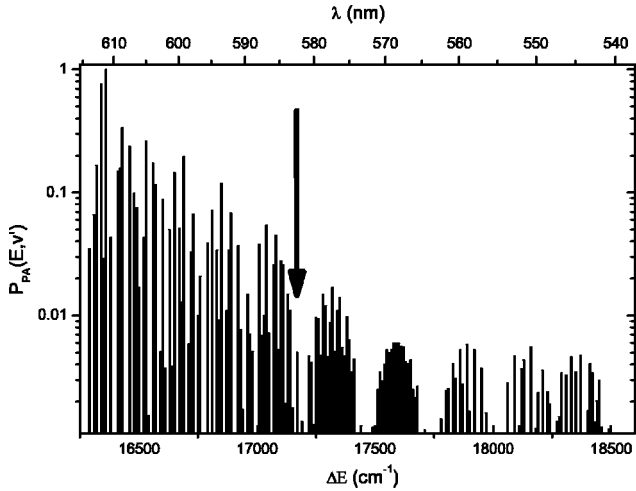
FIG. 2. Normalized transition probability for the $3\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ photoassociation transition as a function of transition energy in wave numbers (bottom) and wavelengths (top). The arrow points at the wavelength for exciting the $v'=94$ level ($\lambda_{air} = 581.75$ nm).

dipole moment $D(R)$ for this transition between $v'(3\,^1\Sigma_u^+)$ and $v''(X\,^1\Sigma_g^+)$ vibrational states, and it is normalized to its maximum value,

$$P_{SE}(v',v'') \propto |\langle v''(X\,^1\Sigma_g^+)|D(R)|v'(3\,^1\Sigma_u^+)\rangle|^2. \quad (2)$$

Similar to the previous figure, in Fig. 3 we took the transition dipole moment function from our previous reference [17], modified as described above. A careful inspection of these figures reveals the double-minimum nature of the upper potential curve. It can be readily seen that the largest probability of transition into the ground state $v''(X\,^1\Sigma_g^+)$ vibrational levels is from the lower vibrational states $v'(3\,^1\Sigma_u^+)$ (v'
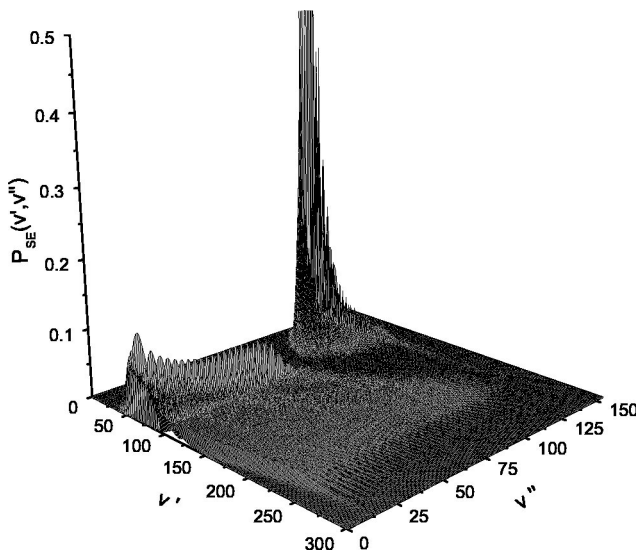

FIG. 3. Normalized transition probability for the spontaneous emission $P_{SE}(v',v'')$ between the upper vibrational level v' in the double-minimum state and the lower vibrational level v'' in the ground electronic state of Cs$_2$.
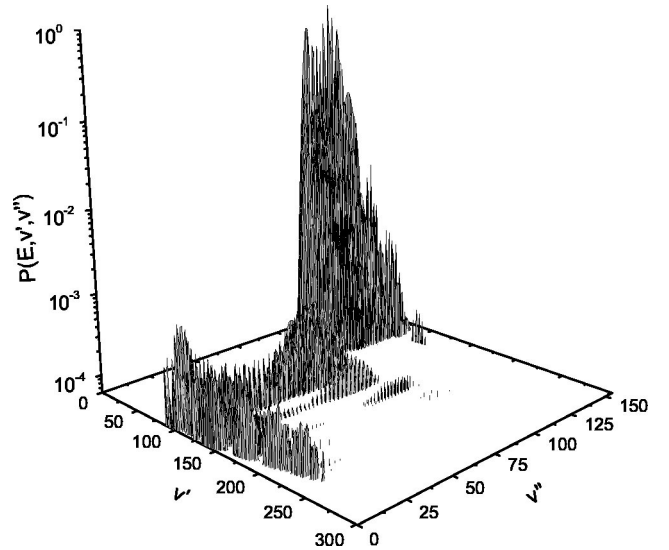

FIG. 4. Normalized probability of ultracold molecule formation, $P(E,v','') = P_{PA}(E,v')P_{SE}(v',v'')$, the product of photoassociation and spontaneous emission as a function of v' and v''.

<100). From vibrational levels above the potential barrier the emission is smaller, but still considerable. The transitions from the outer well region of $3\,^1\Sigma_u^+$ state occur preferentially to higher vibrational states of the $X\,^1\Sigma_g^+$ electronic state, whereas the transitions from the inner well region populate preferentially the lower vibrational levels of the $X\,^1\Sigma_g^+$ electronic state.

In Fig. 4 we present the probability of populating the $v''(X\,^1\Sigma_g^+)$ states as a consequence of photoassociation from the free $\phi(E)$ state into the bound $v'(3\,^1\Sigma_u^+)$ state. This probability $P(E,v',v'')$ is equal to the product of the excitation and the emission transition probabilities, and shows the effectiveness of the ground-state ultracold molecule formation process,

$$P(E,v',v'') = P_{PA}(E,v')P_{SE}(v',v''). \quad (3)$$

We may see that the lowest vibrational levels in the ground electronic state can be populated by exciting vibrational levels of the double-minimum potential around $v' = 100$. However, when exciting only into the outer well of the double-minimum potential, i.e., well below the potential barrier, only very excited vibrational levels in the ground molecular state can be formed.

Finally, we present the calculated values of the product of the excitation and the emission transition probabilities through the $v'=94$ level of the double minimum potential in Fig. 5. This vibrational state lies slightly above the barrier in the double-minimum state and is selected as the most promising level for making the ultracold cesium dimer in $v''=0$, with the overall transition probability nearly twice that of other low-lying vibrational levels.

III. DISCUSSION

Double-minimum potential curves are not isolated phenomena in the realm of alkali dimers. It is known that the
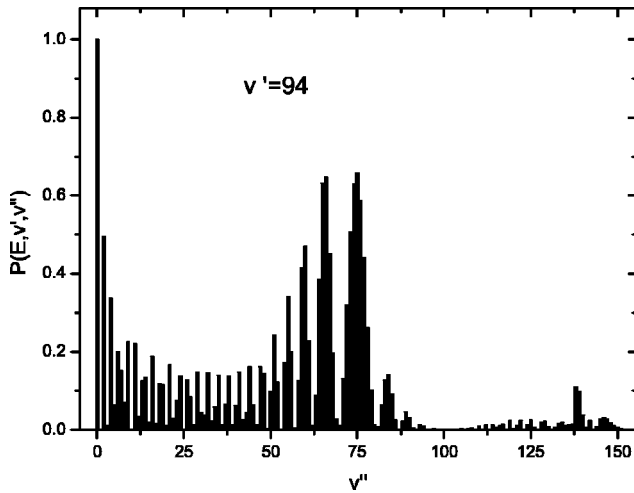
FIG. 5. Normalized probability of ultracold molecule formation expressed as the product of the photoassociation and spontaneous emission probabilities as a function of v'' for the case of $v'=94$.

Cs_2 0_g^- and $1_u(6P_{3/2})$ pure long-range states are actually double-minimum potentials. The outer minima have been indirectly observed as the beginning of asymmetry in the atomic spectral line shape [19] and as pronounced satellite bands [20]. Pillet and co-workers have discussed the advantages of a double-minimum potential for the formation of the ultracold molecules using photoassociation of ultracold cesium atoms in a MOT [21].

The presented scheme shows a high probability for producing molecules in the $v''=0$ level of the Cs_2 $X\,^1\Sigma_g^+$ ground state. Assuming that there is no trapping or other near-resonant light present during the photoassociation process, ultracold MOT conditions allow mostly low partial-wave collisions, which reduce the number of accessible rotational levels in the best cases (s-wave and p-wave) to only $J''=0$ and 2 or $J''=1$, respectively. In the case of a $X\,^1\Sigma_g^+$ (0_g^+) s-wave collision, $\ell=0$, only $J'=1$ is populated, which emits to $J''=0$ and 2. Similarly, in the case of a $X\,^1\Sigma_g^+$ (0_g^+) p-wave collision, $\ell=1$, $J'=0$ or 2 are populated. $J'=0$ emits to $J''=1$ only, whereas $J'=2$ emits to $J''=1$ or 3. Thus, the ground-state molecules formed are extremely cold not only translationally but also vibrationally and rotationally. A more elaborate and complex scheme for direct internal cooling [1] is therefore completely avoided.

Although the singlet $X\,^1\Sigma_g^+$ $(v''=0)$ molecules, unlike the $a\,^3\Sigma_u^+$ triplet molecules, cannot be magnetically trapped, trapping is possible in an optical dipole trap [22]. Using a

high-power CO_2 laser, trap depths of ~1 mK sufficient for trapping ultracold molecules may be realized. A quasistatic optical trap with two crossed CO_2 laser beams was used to obtain Bose-Einstein condensation in the case of ^{87}Rb [23]. Recently, a similar attempt resulted in first achievement of a cesium BEC [24]. This opens the possibility for making a molecular Bose-Einstein condensate (MBEC). A very promising method is one that uses Feshbach resonances. The proposed schemes of making a ground-state MBEC with vibrationally excited molecules [25–28] could be applied to finally produce a MBEC with molecules in the $v''=0$ and $J''=0$ state. If a Feshbach resonance or a nearby state can be taken as an initial state for the excitation to the outer turning points of the double-minimum potential, then we could enormously enhance the probability of the two-photon Raman process shown in Fig. 1, by using resonance-bound or bound-bound excitations into the double-minimum Cs_2 $3\,^1\Sigma_u^+$ state.

IV. CONCLUSION

We have described how the Cs_2 $3\,^1\Sigma_u^+$ state can be exploited for efficient Cs_2 ultracold molecule formation. This scheme can also be used for other ultracold alkali dimers which exhibit similar double-minimum potentials. Ultracold dimers are formed in $v''=0$ of the singlet ground state with only a few quanta of rotational energy ($J''=0,1,2,3$), thus eliminating vibrational relaxation and possible heating. Such molecules present excellent candidates for achieving a pure molecular BEC.

An alternative approach may be realized with the two-photon Raman process. Potentially, such a process may better define the final ground state of molecules and provide higher transfer efficiency by reducing the losses associated with the intermediate state. In addition, the use of double-minimum potential can be extended to heteronuclear alkali molecules [29,30].

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