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Efficient formation of deeply bound ultracold molecules probed by broadband detection

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Using a nonselective broadband detection scheme we discovered an efficient mechanism of formation of ultracold Cs_2 molecules in deeply bound vibrational levels ($v=1-9$) of their electronic ground state $X\,^1\Sigma_g^+$. They are formed by a one-photon photoassociation of ultracold cesium atoms in a manifold of excited electronic states, followed by a two-step spontaneous emission cascade. This process creates about 10^5-10^6 molecules per second. This detection scheme is an advancement compare to previous ones and could be generalized to other molecular species for the systematic investigation of cold molecule formation mechanisms.

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The creation and the study of ensembles of cold and ultracold molecules attract considerable attention [1–4]. The only way to produce molecules with a temperature in the sub-milli-Kelvin range relies on the association of ultracold atoms using, for instance, magnetoassociation, via Feshbach resonances in quantum degenerate gases [5–9], or photoassociation (PA) of ultracold atoms from a standard magneto-optical trap (MOT) [10]. PA is a well-known efficient process for the formation of ultracold molecules, with a rate as high as $\sim 10^6-10^7$ s^{-1}. The main drawback of the PA approach is the spread of the population of the formed molecules over many vibrational levels v with low binding energy. Nevertheless, ultracold ground-state K_2 molecules created in the lowest vibrational level $v=0$ have been observed via a two-step PA scheme [11], while a sequence of a PA step followed by an absorption-emission transfer have produced ultracold ground-state RbCs molecules in $v=0$ as well [12]. Ultracold ground-state LiCs molecules in the absolute rovibrational level $v=0$, $J=0$ (v the vibrational quantum level and J the rotational one) have also been detected after a single PA step [13]. However, in all these experiments the formation rate is limited to $\sim 10^3$ s^{-1} molecules in $v=0$.

As published previously [14], an optical pumping technique using a tailored broadband light source, allowed us to form about 10^5-10^6 molecules per second in the $v=0$ level of the ground state. The method relies on an efficient PA formation scheme yielding molecules in $v<10$ levels. In this Rapid Communication, we emphasize the tool which has been used to find this efficient PA formation scheme. Indeed, it is generally a considerable task to discover novel PA schemes. Such schemes generally involve peculiarities of the electronic structure of each individual molecular species: potential barrier [15,16], shape [17], or Feshbach [18] resonances in the ground state, nonadiabatic couplings in the PA state [19], flux enhancement [20], or accidental matching of radial wave functions related to each step of the process [11].

In this Rapid Communication we demonstrate a general and systematic method to look for efficient ultracold molecule formation schemes based on PA, which requires only basic knowledge of the molecular structure. It is based on a detection procedure which does not select the population of a particular bound level of the formed molecules, in contrast with all previous experiments relying on resonantly enhanced multiphoton ionization (REMPI) [10].

PA of cold cesium atoms [21] is achieved with a cw titanium:sapphire laser (intensity 300 W cm^{-2}), pumped by an argon-ion laser, exciting molecules which can decay by spontaneous emission into vibrational levels of the molecular ground state $X\,^1\Sigma_g^+$ (hereafter referred to as X), or of the lowest triplet state $a\,^3\Sigma_u^+$. In order to observe deeply bound molecules in the X state, which could result from an *a priori* unknown mechanism, we set up a broadband REMPI detection through vibrational levels v_B of the spectroscopically known $B\,^1\Pi_u$ excited state [22] (referred to as the B state). The two-photon transition is induced by a pulsed dye laser (LDS751 dye, wavelength $\sim$770 nm, pulse energy $\sim$1 mJ, focused waist $\sim$500 μm) and by the pump laser (532 nm wavelength) as illustrated in Fig. 1(a). The formed Cs_2^+ ions are then detected using a pair of microchannel plates after passing through a time-of-flight mass spectrometer.

The major advance of the present experiment compared to previous ones is the broadband detection of the formed ultracold molecules. We replaced the grating in the pulsed dye laser cavity by a less dispersive prism, which broadens its linewidth from $\sim$0.05 to $\sim$25 cm^{-1} (measured using a HP-86142A Optical Spectrum Analyzer). We display in Fig. 1 the results of a modeling of the ionization process, for both narrow-band (panel b) and broadband (panel c) schemes. We assume that the ionization probability is proportional to the population of the v_B level induced by the first photon at 770 nm. The excitation probabilities of the v_X levels toward the v_B levels are obtained from Franck-Condon factors computed for the experimentally known X and B potential curves [22,23], assuming a constant transition dipole moment. As expected, the narrow-band ionization scheme allows for the ionization of a single v_X level at a given frequency [Fig. 1(b)]. In contrast, the broadband scheme involves a laser pulse width of the order of the vibrational spacing of both the X and B states (up to 40 cm^{-1}), so that many vibrational v_X

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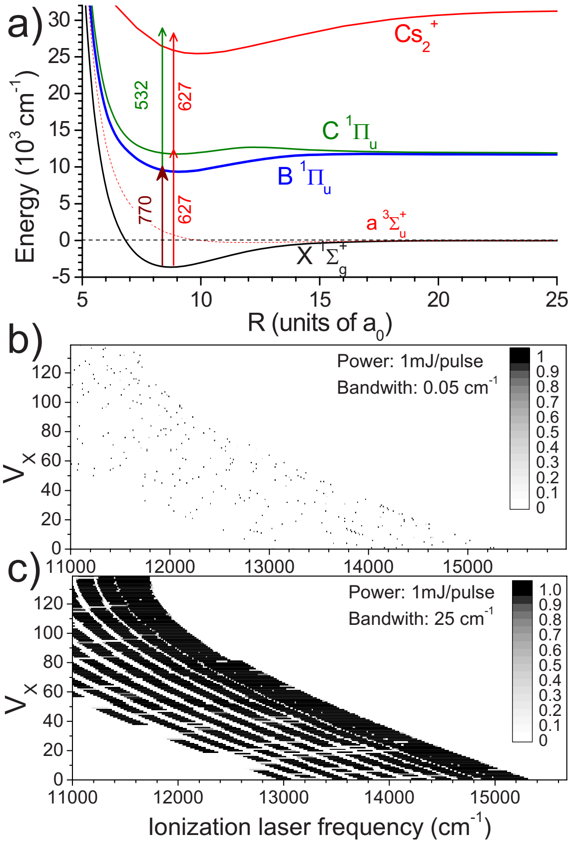

FIG. 1. (Color online) (a) REMPI detection scheme of deeply bound ground-state Cs_2 molecules with a broadband laser at 770 nm (with an extra laser at 532 nm) via the $B\ ^1\Pi_u$ state, and with a narrow-band laser at 627 nm via the $C\ ^1\Pi_u$ state. Transition probabilities of the ground-state vibrational levels v_X toward levels of the B state, as functions of their energy difference E_{X-B} for a laser linewidth of 0.05 cm^{-1} (b) and of 25 cm^{-1} (c), with identical power (1 mJ/pulse). The probability is put to unity for a saturated transition.

levels can be ionized in a single shot [Fig. 1(c)]. For instance, a laser pulse at ~11 730 cm^{-1} or at ~13 000 cm^{-1} would saturate the excitation of almost all molecules in vibrational levels $v_X > 37$ or $v_X < 70$, respectively.

Choosing the frequency of the first laser around 13 000 cm^{-1} we then scanned the PA laser frequency over a few wave numbers below the $6s+6p_{3/2}$ dissociation limit. We discovered several intense PA lines labeled with crosses in Fig. 2, revealing a large number of ultracold molecules formed in low ($v_X < 70$) vibrational levels of the X state. These detected singlet molecules were actually present in our previous experiments performed in the same PA energy range [21], but our previous narrow-band REMPI detection scheme (wavelength ~720 nm) was optimized to detect $a\ ^3\Sigma_u^+$ molecules, and therefore was blind to these singlet molecules (see lower part of Fig. 2).

To precisely determine the internal state of these formed molecules we fix the PA laser energy on the most intense line of Fig. 2 and we performed conventional narrow-band REMPI to record the ionization spectrum through the intermediate $C\ ^1\Pi_u$ state [23,24]. The lines (shown in Fig. 3) are easily assigned to transitions from ground-state vibrational levels restricted to the range $v_X=1$ to $v_X=9$. Taking into account the efficiency of the detection [14,21], the ion signal corresponds to a cumulative formation rate for the $v_X < 10$ molecules close to 10^6 per second.

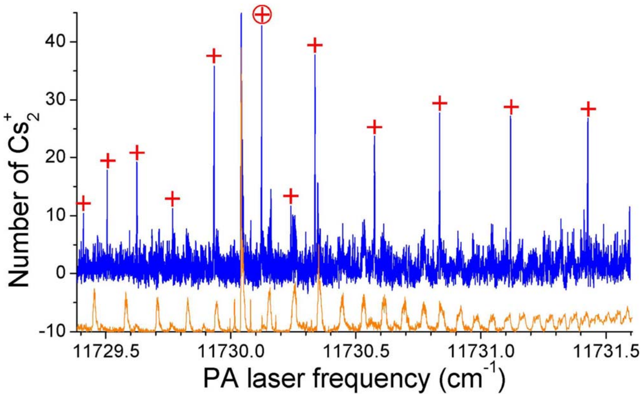

FIG. 2. (Color online) Upper trace: Cs_2^+ ion spectrum recorded after scanning the frequency of the PA laser below the $6s+6p_{3/2}$ dissociation limit, and using the broadband REMPI detection laser with energy around 13 000 cm^{-1}. The crosses label the previously unobserved PA lines. Lower trace: Cs_2^+ ion spectrum obtained using the conventional narrow-band REMPI detection with energy around 13 900 cm^{-1} (optimized to detect $a\ \Sigma_u^{+3}$ molecules) [21], displayed with an offset of ten ions for clarity.

In order to further investigate this novel efficient PA mechanism, we improved the PA signal of Fig. 2 by (i) performing a vibrational cooling step, which accumulates the $v_X < 10$ population into the sole $v_X=0$ level [14] and (ii) by detecting these molecules using the narrow-band detection through the known transition between $X(v_X=0)$ and $C(v_C=0)$. The PA spectroscopy performed under such con-

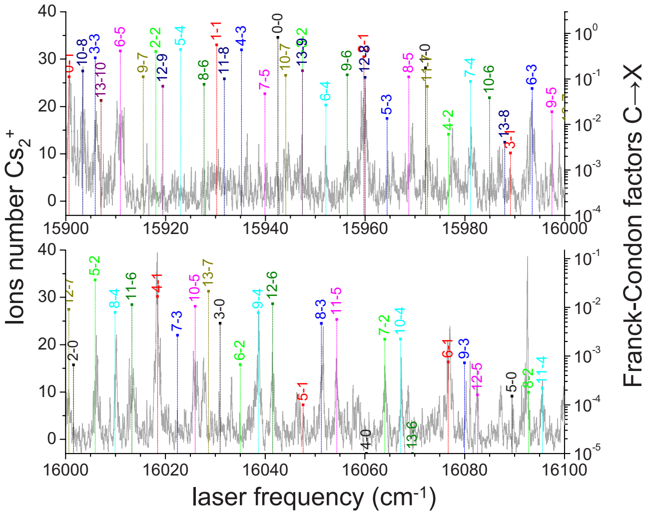

FIG. 3. (Color online) Cs_2^+ ion count (left vertical axis) resulting from a standard (narrow-band) REMPI detection [frequency ~627 nm see Fig. 1(a)]. The PA laser energy is fixed at 11 730.1245 cm^{-1} corresponding to the line marked with a circled cross in Fig. 2. Transition labels $v_C - v_X$ are extracted from the spectroscopically known C and X states and the transition strength is computed using the known Franck-Condon factors (right vertical axis).

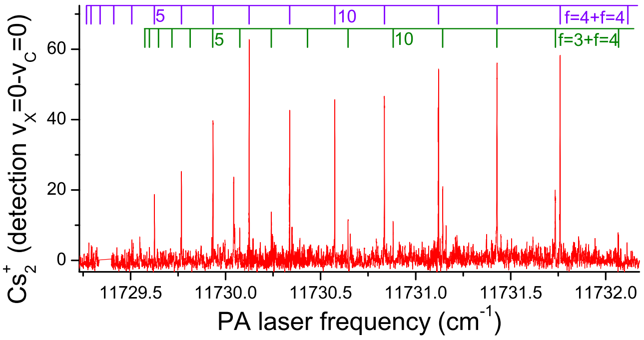

FIG. 4. (Color online) Same as Fig. 2 but Cs_2^+ ions are now detected with a narrow-band laser (wave number 15 941 cm^{-1}) tuned to resonance with the transition $(v_X=0)\rightarrow(v_C=0)$ and an additional vibrational cooling step is performed [14]. An intense series and a weak rotational series, separated by 9.2 GHz have been fitted, assigned to rotational levels from $J=5$ to 14. Extrapolated line positions for $J=0$–4 are also displayed.

ditions is depicted in Fig. 4. Two series of lines separated by 9.2 GHz (i.e., the hyperfine splitting between the $f=3$ and $f=4$ cesium $6s$ states, where f is the total angular momentum) are visible. As the MOT mainly contains Cs($f=4$) atoms, the intense lines correspond to PA of two Cs($f=4$) atoms, and the weak lines to PA of one Cs($f=4$) and one Cs($f=3$) atom. This 9.2 GHz line spacing rules out the possibility that the molecules are formed after a PA step with two identical photons, as this would induce a spacing twice smaller. The series of intense lines is easily assigned to a rotational progression with rotational quantum number between $J=5$ and 14. We fitted a rotational constant $B_v=0.01188(1)$ cm^{-1}, corresponding to an approximate average internuclear distance $\bar{R}_0\equiv(2\mu B_v)^{-1/2}=8.73a_0$, where μ is the Cs_2 reduced mass ($a_0=0.0529177$ nm). Thus this novel single-photon PA mechanism excites both [Cs($f=4$), Cs($f=4$)] and [Cs($f=4$), Cs($f=3$)] ground-state atom pairs, into a level located about 2 cm^{-1} below the $6s+6p_{3/2}$ asymptote, with a vibrational motion taking place mainly in the short-distance range. A similar situation of an efficient long-range PA followed by spontaneous emission at "short" distance, has already been demonstrated for the lowest 0_u^+ excited states in Cs_2 and is induced by internal couplings between potential curves [19]. Relying on theoretical Cs_2 potential curves including spin orbit [25,26], we identified only one excited potential curve, belonging to the 1_g symmetry, as a good candidate for the PA state. We depict the process as follows: the PA laser excites the atom pair into a bound level of the lowest $1_g(6s+6p_{3/2})$ long-range potential curve (curve 1 in Fig. 5), which is coupled at short distances to the lowest $1_g(6s+6d_{5/2})$ potential curve (curve 4 in Fig. 5), through several avoided crossings induced by spin-orbit interaction. The $v=0$ level of the curve 4 is predicted with an energy very close to the $6s+6p_{3/2}$ dissociation energy. It is most probably the only populated short-range level in this mechanism, which then decays down to the X ground state through a two-photon spontaneous emission cascade via the 0_u^+ potentials. Note that the spontaneous decay cannot directly proceed down to the levels of the $a\,^3\Sigma_u^+$ state, as the average distance $8.73a_0$ corresponds to the range of the repulsive wall so that only dissociating pairs could be formed. Preliminary simulation of the two-photon spontaneous emission cascade based on Franck-Condon factors indeed indicates population of vibrational level $v_X<10$, as observed experimentally, but also population of levels $v_X\sim 40-70$, which are not observed experimentally probably because of their poor REMPI probabilities.

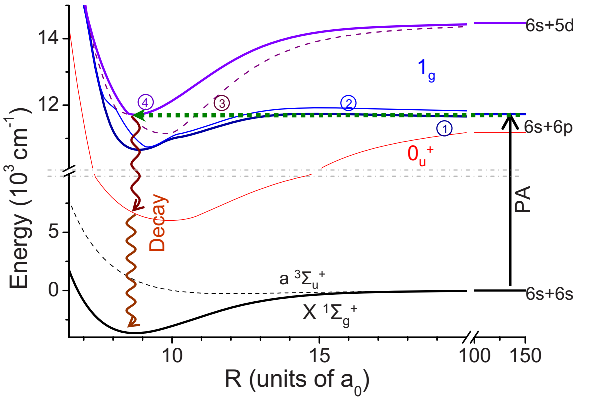

FIG. 5. (Color online) Theoretical Cs_2 molecular potential curves including spin orbit [25,26], relevant for the present PA and cold molecule formation process. The PA laser excites levels of a long-range 1_g curve (label 1), which is coupled to the $v=0$ level of the short-range 1_g curve (label 4) through several avoided crossings involving 1_g curves labeled 2 and 3. Formation of a deeply bound ground-state molecule proceeds through a spontaneous emission cascade via the 0_u^+ states.

To investigate the reason for the presence of high values of the rotational quantum number (up to $J=14$) of the PA molecules, we turned off the MOT lasers 2 ms before switching on the PA laser, and while the PA laser was on (1 ms). We observed no change in the PA spectrum. This demonstrates that the MOT lasers (both trapping and repumping ones) do not bring additional angular momentum into the process, in contrast to previous observations in sodium PA where lines up to $J=22$ have been reported [27], or in cesium PA where lines up to $J=8$ have been reported [28]. Such high J values are probably induced by the large hyperfine structure of the long-range $1_g(6s+6p_{3/2})$ state [10]. A strong mixing between hyperfine and rotational structure is expected, just as in the well-studied $1_u(6s+6p_{3/2})$ Cs_2 molecular state [29]. The $1_g(6s+6p_{3/2})$ levels are characterized by a value of the total angular momentum $\mathbf{F}=\mathbf{J}+\mathbf{I}$, where $\mathbf{I}$ is the total nuclear angular momentum ($I\leqslant 7$) of a cesium atom pair. The PA excitation of nonrotating ground-state atom pairs, which takes place at large distances, creates a strongly mixed hyperfine-rotational level of the $1_g(6s+6p_{3/2})$ state with $F\sim I\leqslant 7$. Due to the high density of levels near the dissociation threshold, this PA level can be efficiently coupled to several rotational states of the $v=0$ level of the internal $1_g(6s+6d_{5/2})$ potential curve. The rotational angular momentum $\mathbf{J}=\mathbf{F}-\mathbf{I}$ can reach eigenvalues up to $J=14$ or more. The abrupt cutoff of the observed rotational series at $J=14$ in Fig. 4 occurs as the next rotational levels lie above the $6s+6p_{3/2}$ dissociation limit.

In this Rapid Communication we demonstrated the ability of a broadband ionization procedure to detect most of the ground-state molecules formed in a cold gas. This approach, which requires only a basic knowledge of the excitation spectrum of the ground state, provides a general method for the search of novel paths for formation of cold molecules by photoassociation. This allowed us to detect deeply bound Cs_2 molecules in the $X\,^1\Sigma_g^+$ state. The simplicity of the experiment (one-step photoassociation) contrasts with the complexity of the interpretation of the photoassociation process, which involves, rotational, hyperfine, and spin-orbit couplings of four potential curves. The formation process also revealed an unexpected two-photon spontaneous emission cascade responsible for the molecule formation. This scheme opens the possibility to stimulate the first photon of the cascade to enhance the cold molecule formation rate. In the future such molecules could be accumulated in an optical trap to study collisional processes between cold atoms and molecules in order to assess the efficiency of evaporative cooling, or to investigate ways for achieving controlled chemistry or observing dipolar interactions in ultracold gases.

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