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Optical Pumping and Vibrational Cooling of Molecules

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The methods producing cold molecules from cold atoms tend to leave molecular ensembles with substantial residual internal energy. For instance, cesium molecules initially formed via photoassociation of cold cesium atoms are in several vibrational levels ν of the electronic ground state. We applied a broadband femtosecond laser that redistributes the vibrational population in the ground state via a few electronic excitation/spontaneous emission cycles. The laser pulses are shaped to remove the excitation frequency band of the $\nu = 0$ level, preventing re-excitation from that state. We observed a fast and efficient accumulation (~70% of the initially detected molecules) in the lowest vibrational level, $\nu = 0$, of the singlet electronic state. The validity of this incoherent depopulation pumping method is very general and opens exciting prospects for laser cooling and manipulation of molecules.

Over the past 20 years, the field of atomic physics has made enormous strides, with laser cooling and the achievement of atomic Bose-Einstein condensation. Similar advances are expected with cold molecules, involving applications, for instance, in molecular clocks, tests on fundamental physical constants, or quantum computing. Thus, the preparation of dense molecular samples in the ground state at low temperatures offers exciting prospects in both physics and chemistry (*1*–*3*).

An important step in the field of cold molecules has been the demonstration of a method for producing translationally cold samples of ground-state Cs_2 molecules via photoassociation of cold Cs atoms (*4*). This result has been quickly followed by the elaboration of various methods to prepare cold molecular samples. Methods that start with pre-formed molecules, usually in the lowest vibrational level, access translational temperatures down to a few millikelvins (*5*–*9*). Accessing temperatures even lower than these presents a major challenge. Cold molecules in the micro- or nanokelvin temperature range can only be achieved starting with cold atoms using collisional processes such as photoassociation in a thermal atomic cloud (*4*), Feshbach magnetoassociation in atomic Bose-Einstein condensates (*10*), or three-body collisions in an atomic Fermi sea to prepare molecular Bose-Einstein condensates (*11*). However, these methods of producing (translationally) cold molecules from cold atoms lead to the production of vibrationally excited molecules; that is, those with residual internal energy. For additional applications of cold molecules (*1*–*3*), the challenge is therefore to prepare and control molecules in the ground vibrational and rotational state.

Various experimental schemes can favor the formation of cold molecules in their lowest vibrational level. In a quantum gas, the adiabatic transfer of population [stimulated Raman adiabatic passage (STIRAP)] from a high ro-vibrational level toward a lower one has been achieved recently for molecules formed by magnetoassociation (*12*). In a cold thermal gas, a fraction of cold ground state Rb-Cs molecules, initially formed by photoassociation, has been prepared into the lowest vibrational level, $\nu = 0$, with a rate of ~500 s^{-1} by transferring ~6% of the population of a given high vibrational level into $\nu = 0$ (*13*). A few $\nu = 0$ cold ground-state potassium dimers have also been observed with the use of a two-photon process for photoassociation (*14*), but several other vibrational levels are populated as well. For further applications, what is needed is a molecular analog of optical pumping of atoms to realize vibrational laser cooling, which would transfer all the populations of the different vibrational levels into the lowest one.

Several theoretical approaches have been proposed to favor spontaneous emission toward the lowest ro-vibrational level: for instance, the use of an external cavity (*15*) or controlled interplay of coherent laser fields and spontaneous emission through quantum interferences between different transitions (*16*–*18*). As in these latter coherent control propositions, our approach uses a shaped pulsed laser but is based on an incoherent process of depopulation pumping with a train of several identical weak femtosecond laser pulses. More closely related to our work is the proposition of using a tailored incoherent broadband light source for the rotational cooling of molecular ions (*19*, *20*).

Here, we report the transfer of populations from an ensemble of vibrational levels of cold Cs_2 molecules, prepared in the electronic ground-state via photoassociation, into $\nu = 0$. The main idea is to use a broadband laser tuned to the transitions between the different vibrational levels (labeled ν_X and ν_B) of the singlet-ground-state X and an electronically excited state B. The absorption/spontaneous emission cycles lead, through optical pumping, to a redistribution of the vibrational population into the ground state (Eq. 1)

$$Cs_2(\nu_X) + h\nu \longrightarrow Cs_2(\nu_B) \xrightarrow{\text{decay}} Cs_2(\nu'_X) \quad (1)$$

where ideally $\nu'_X < \nu_X$ to realize vibrational cooling. The broadband character of the laser permits repetition of the pumping process from multiple vibrational states. By removing the laser frequencies corresponding to the excitation of the $\nu_X = 0$ level, we make it impossible to pump molecules out of this level, thus making $\nu_X = 0$ a dark state. As time progresses, the absorption/spontaneous emission cycle described by Eq.

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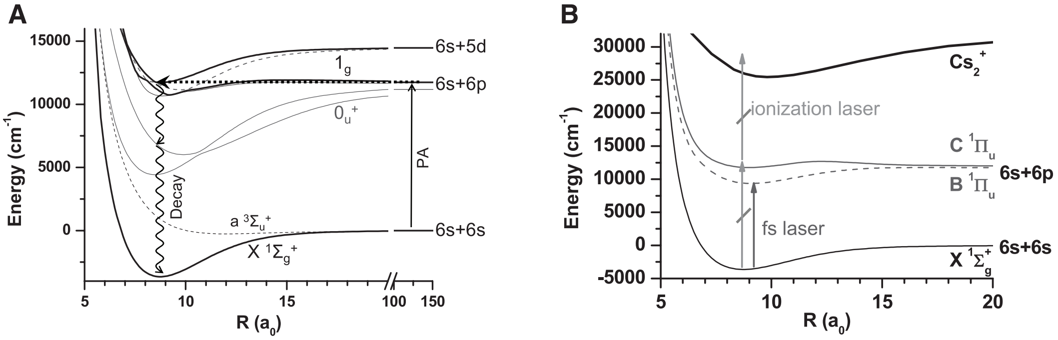

Fig. 1. Relevant schematic molecular potential curves of the Cs dimer, converging toward the dissociation limits 6s+6s, 6s+6p, and 6s+5d (for clarity, the fine structure is not labeled). (**A**) Photoassociation of cold atoms and formation of cold molecules. The cw laser (PA) is tuned ~1 cm^{-1} below the atomic transition $6s_{1/2} \longrightarrow 6p_{3/2}$. For the potentials of 1_g symmetry, long-range radial wave function is coupled to short range radial wave function by internal coupling of the potentials (*26*). The ground-state molecules, $X^1\Sigma_g^+$, are formed by a spontaneous emission cascade via the 0_u^+ potentials. (**B**) REMPI ionization process via the $C^1\Pi_u$ state by the pulsed dye laser, and electronic transition $X^1\Sigma_g^+$ toward $B^1\Pi_u$ induced by the femtosecond laser. a_0 is the Bohr radius.

1 leads to an accumulation of the molecules in the $\nu_X = 0$ level. We thereby realize vibrational laser cooling.

In our experiment, the formation of cold molecules is achieved in a Cs vapor-loaded magneto-optical trap (MOT) via photoassociation (*4*). Two colliding cold atoms resonantly absorb a photon with a frequency tuned slightly (~1 cm^{-1}) below the atomic $6s_{1/2} - 6p_{3/2}$ transition to create a molecule in an excited electronic state. The photoassociated molecules decay by spontaneous emission into stable vibrational levels of the molecular ground state $X^1\Sigma_g^+$ (Fig. 1A). They are then detected by resonance enhanced multiphoton ionization (REMPI). In contrast with previous studies (*4*), the REMPI frequency is tuned to ionize deeply bound vibrational levels of the X state through the excited $C^1\Pi_u$ molecular state (Fig. 1B). The complete mechanism for the formation of cold molecules in the singlet ground state is currently being studied, but the most probable scenario is shown in Fig. 1A. Photoassociation is achieved using a cw Titanium:Sapphire laser (intensity = 300 W cm^{-2}) pumped by an Argon-ion laser. The REMPI detection uses a pulsed dye laser (wave number ~ 16000 cm^{-1}, spectral bandwidth = 0.3 cm^{-1}) pumped by the second harmonic of a pulsed Nd:YAG (Nd–yttrium-aluminum-garnet) laser (repetition rate = 10 Hz, duration = 7 ns). The formed Cs_2^+ ions are detected with a pair of microchannel plates through a time-of-flight mass spectrometer. In the experimental spectrum obtained by scanning the REMPI laser wavelength (Fig. 2A), we assigned the observed lines to known transitions from the ground state levels $\nu_X = 1$ to 7 to various levels of the C state (*21*). In this first step, no molecules in the vibrational level $\nu_X = 0$ are detected. The present low REMPI resolution does not provide the capability of analyzing the rotational population of the molecules.

To achieve vibrational cooling, we applied a broadband femtosecond mode-locked laser (repetition rate = 80 MHz, pulse duration = 100 fs, SD-Gaussian bandwidth = 54 cm^{-1}, average intensity = 50 mW/cm^2, and central wavelength = 773 nm or wave number = 12,940 cm^{-1}) tuned to the electronic transitions from $X^1\Sigma_g^+(\nu_X)$ to $B^1\Pi_u(\nu_B)$ (Fig. 1B). Without shaping the femtosecond laser pulses, we observe a modification of the vibrational distribution, which we interpret as a transfer of population between vibrational levels as indicated by Eq. 1. The relative strengths of the transitions between the vibrational levels of the X-B states are given by the Franck-Condon factors (Fig. 3B). If we consider, for instance, a molecule in $\nu_X = 4$, the most probable excitation is to $\nu_B = 1$, which decays as in Eq. 1 with a partitioning ratio of ~30% to $\nu'_X = 0$ and 70% distributed essentially among ν'_X = 3, 4, and 5. To control the optical pumping of the molecules, we shaped the femtosecond laser pulses by suppressing the frequencies above 13,030 cm^{-1} that could induce electronic excitation from $\nu_X = 0$ (Fig. 3A and hatched area in Fig. 3B). We used a home-built shaper with a diffraction grating (1800 lines/mm) after which high frequencies of the laser beam are screened out (lower part of Fig. 3A). After a few cycles of absorption of laser light and spontaneous emission, considering the populations in the observed vibrational levels ($\nu_X = 0 - 10$), a large fraction (65 ± 10%) of the molecules are accumulated in the lowest vibrational level ($\nu_X = 0$).

On application of the shaped laser pulses, the resonance lines corresponding to transition from $\nu_X = 0$ to $\nu_C = 0$ to 3 emerged strongly in the

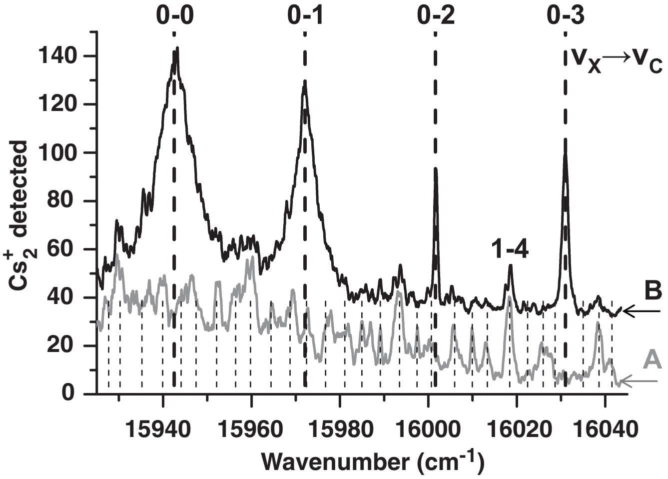

Fig. 2. Cs_2^+ ion spectra. (**A**) Spectrum without the shaped laser pulse. The spectrum has a background due to other REMPI processes that do not mask the resonance lines. Vertical dashed lines indicate the positions of all the resonances for vibrational transitions between the ground state, $X^1\Sigma_g^+$ (ν_X = 0 to 7) and the electronically excited $C^1\Pi_u$ state (ν_C). (**B**) Spectrum with the shaped laser pulse applied continuously, offset by 40 ions for higher visibility. The observed transitions from $\nu_X = 0$ correspond to ν_C = 0, 1, 2, and 3. Their broadening corresponds to the saturation of the resonance in the REMPI process. Most of the lines present in spectrum (A) are greatly reduced, whereas the $\nu_X = 0$ lines grow more intense. The resonance labeled 1-4 indicates imperfect depopulation of $\nu_X = 1$ because of the roughness of the shaping.

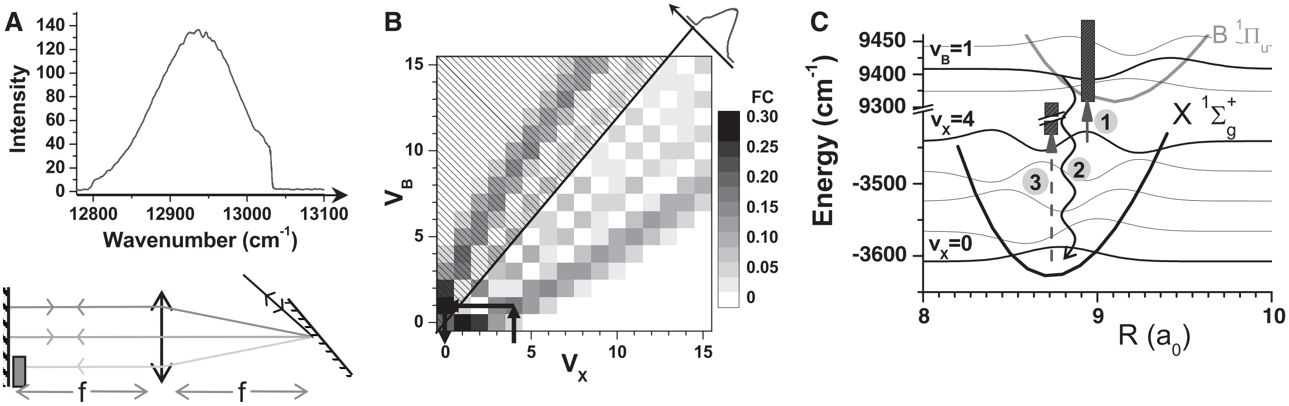

Fig. 3. Optical pumping scheme with a shaped femtosecond laser pulse. (**A**) (Top) Line gives the laser spectrum profile with shaping [also shown in (B)], close to a Gaussian profile sharply cut off at 13,030 cm^{-1}. (Bottom) 4-*f* shaping arrangement (from right to left: grating, cylindrical lens *f* = 500 mm, blocker, mirror). (**B**) Condon parabola indicating the importance (level of gray) of the Franck-Condon (FC) factors (square of the wave function overlap), corresponding to the relative transition probabilities from ν_X to ν_B. The diagonal line corresponds to the shaped laser cutoff frequency (13,030 cm^{-1}). The hatched area cannot be accessed in the presence of the blocker. (**C**) Optical pumping scheme and vibrational wave functions. The vertical black boxes indicate the spectral bandwidth of the laser. In (B) and (C), arrows indicate the optical pumping for $\nu_X = 4$ molecules. The most probable optical pumping scheme is to reach $\nu_X = 0$ through excitation into $\nu_B = 1$. Step 1, excitation toward $\nu_B = 1$; step 2, spontaneous decay to $\nu_X = 0$; and step 3, molecules in $\nu_X = 0$ are trapped. The incoherent dark state formed by the laser pulse shaping does not allow the excitation from $\nu_X = 0$ to any ν_B level.

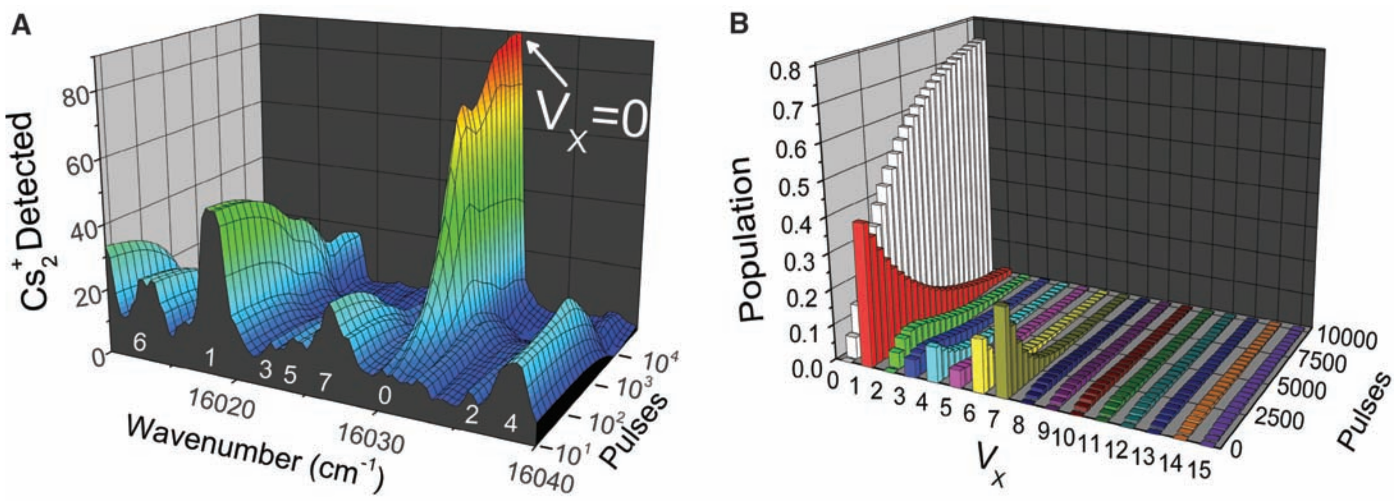

Fig. 4. Temporal evolution (pulse separation = 12.5 ns) of the populations in the different vibrational levels of the ground state. Because of our weak laser intensity, the excitation probability is only 0.1% for a single pulse. (**A**) Experimental population versus the number of applied femtosecond pulses, smoothed from five spectra (similar to Fig. 2 but taken after a controlled number of pulses). The frequencies correspond to transitions from $\nu_X = 0-7$ to ν_C levels (white label). (**B**) Theoretical simulation where we represent the temporal evolution of $\nu_X = 0$ to 15 starting with initial conditions close to the experimental ones.

REMPI spectra (Fig. 2B). The intensity of the lines indicates efficient transfer of the molecules into the lowest vibrational level $\nu_X = 0$. By controlling the number of femtosecond laser pulses with an acousto-optic modulator, we analyzed the time dependence of the optical pumping scheme (Fig. 4A). At the weak laser intensities applied here, the transfer of population into the $\nu_X = 0$ level is almost completed after an exposure of the sample to 5000 pulses over 60 µs. Taking into account the efficiency of the detection, the detected ion signal corresponds to about 1000 molecules in the $\nu_X = 0$ level in the MOT area and thus to a formation rate of $\nu_X = 0$ molecules of more than 10^5 per second, which represent roughly 1% of the atomic loading flux in the MOT.

We have modeled the optical pumping process using the experimentally known $X^1\Sigma_g^+$ and $B^1\Pi_u$ potential curves (*22*, *23*). In our perturbative regime, the excitation probabilities are proportional to the laser spectral density at the transition frequencies. The lifetime of the electronically excited state B (~15 ns) is close to the 12.5-ns repetition period of the femtosecond laser, leaving negligible accumulation of coherence in the sample from pulse to pulse (*24*). We then assumed in our rate equation model an instantaneous spontaneous decay. The model shows that the vibrational population (ν_X) proceeds by random walk, mostly through low vibrational levels, until reaching the $\nu_X = 0$ level. More than 70% of the total population is transferred into the $\nu_X = 0$ level (Fig. 4B) when we start from a distribution of vibrational levels close to the experimental one. The simulation shows that the limitation of the efficiency of the mechanism is in the optical pumping toward higher vibrational levels. Nevertheless, the simulation demonstrates that, for instance, increasing the bandwidth of the laser would reduce this detrimental pumping and would increase the population in $\nu_X = 0$. The theoretical model agrees well with the data in Fig. 4A. Furthermore, it indicates that only about five absorption/spontaneous emission cycles, corresponding to ~5000 laser pulses, are necessary for a molecule to be transferred into the $\nu_X = 0$ level. This small number of cycles does not substantially modify the temperature of the molecular sample. The theoretical simulation takes into account the rotational levels and demonstrates, for the experiment, the possibility to achieve rotational cooling for an adapted shaping, accurate enough to resolve the rotational structure.

The method—optical pumping of diatomic molecules using a shaped broadband source—is expected to be generally applicable to most molecular sample experiments that present a distribution of population of the low vibrational levels in the ground state. The efficiency will depend on the transition strengths between the different vibrational levels of the considered electronic states, but it could be optimized with a suitable shaping. The optical pumping should not be limited to cold samples of molecules prepared via photoassociation of cold atoms but should also be applicable to other cases, such as molecules in a molecular beam. Broadband shaped optical pumping could also be used as a repumping laser in laser manipulation of atoms and molecules, opening prospects in laser cooling of new species (*25*).

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