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Producing translationally cold, ground-state CO molecules

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Carbon monoxide molecules in their electronic, vibrational, and rotational ground state are highly attractive for trapping experiments. The optical or ac electric traps that can be envisioned for these molecules will be very shallow, however, with depths in the sub-milliKelvin range. Here, we outline that the required samples of translationally cold CO ($X^1\Sigma^+$, $v'' = 0$, $N'' = 0$) molecules can be produced after Stark deceleration of a beam of laser-prepared metastable CO ($a^3\Pi_1$) molecules followed by optical transfer of the metastable species to the ground state *via* perturbed levels in the $A^1\Pi$ state. The optical transfer scheme is experimentally demonstrated and the radiative lifetimes and the electric dipole moments of the intermediate levels are determined. © 2011 American Institute of Physics. [doi:10.1063/1.3637037]

I. INTRODUCTION

During the last decades, researchers have learned to gain ever better control over the internal degrees of freedom and the translational motion of molecules, and a wide variety of molecules have been trapped by now in electric, magnetic, or optical fields.^{1,2} The lowest temperatures and the highest densities have been obtained for molecules that are assembled from their laser-cooled atomic constituents, e.g., for homo- and hetero-nuclear alkali dimers.^{3,4} Cooling and trapping of pre-existing molecules often involves highly reactive species that are produced, for instance, via laser ablation or photodissociation of a precursor molecule. The production efficiency of such radical species limits the absolute number and the number density that can be reached for trapped samples. In a cooling and trapping experiment, one would ideally like to use a stable molecule that is available in a bottle at high vapor pressure. Among all the molecules that have been trapped so far, only ammonia,⁵ carbon monoxide,⁶ and molecular hydrogen⁷ fall in this category. However, the various symmetric top isotopologues of ammonia that have been trapped have a rather complicated energy-level structure due to the presence of four atoms with nonzero nuclear spin. Even the simplest isotopologue, $^{15}\text{NH}_3$, has its population distributed over $12|M_F|$ components when it is trapped in its electronic, vibrational, and rotational ground state by means of electric fields. The CO molecules have thus far only been trapped in their metastable $a^3\Pi$ state. In this open-shell electronically excited state, electrostatic trapping is possible by virtue of the electric dipole moment of +1.37 D together with the first-order Stark interaction, but phosphorescence back to the ground state limits the trapping time to the millisecond range.⁶ Similarly, H_2 molecules have thus far only been trapped in short-lived Rydberg states.^{7,8}

Carbon monoxide in its electronic, vibrational, and rotational ground state ($X^1\Sigma^+$, $v'' = 0$, $N'' = 0$) is in many ways an ideal candidate for trapping experiments. The six stable CO isotopologues combining ^{12}C or ^{13}C with ^{16}O , ^{17}O , or ^{18}O are all commercially available. The most abundant isotopologue $^{12}\text{C}^{16}\text{O}$ is a boson with no nuclear spin. The non-degenerate $N'' = 0$ level is separated by almost 4 cm^{-1} from the next, $N'' = 1$, level. Contrary to the case of many diatomic hydrides,⁹ CO is quite immune to blackbody radiation; even at room temperature, the rate at which the molecules are optically pumped out of the $N'' = 0$ level by blackbody radiation is below 10^{-3} s^{-1} . The $^{12}\text{C}^{18}\text{O}$ isotopologue is also a boson with no nuclear spin, while $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ are fermions with an $F'' = 1/2$ ground level ($\vec{F} = \vec{N} + \vec{I}$ with \vec{I} being the nuclear spin), which remains a single (doubly degenerate) level in the presence of an electric field.

Ground-state CO molecules can in principle be trapped in an ac electric field trap or in an optical trap, although it is an experimental challenge to make a trap with a significant depth. The lowest rotational levels of the electronic ground state of CO have a purely quadratic Stark shift in electric fields that can be realized in the laboratory. The main contribution to the Stark shift is due to the electric dipole moment of -0.1098 D ,¹⁰ although the isotropic polarizability of the ground state¹¹ cannot be neglected. Note that we use here the convention that a positive sign of the dipole moment corresponds to the situation C^+O^- , i.e., in the ground-state the situation is C^-O^+ . The inset of Fig. 1 shows the calculated Stark shifts of the three lowest rotational levels of $^{12}\text{C}^{16}\text{O}$ for electric fields up to 100 kV/cm . It is interesting to note that the acceleration experienced in electric fields by the CO molecules in the $N'' = 0$ level is almost identical to that experienced by ground-state ^{87}Rb atoms. Therefore, the performance of an ac electric trap for ground-state CO molecules will be very similar to that of an ac electric trap for ground-state ^{87}Rb atoms. The latter

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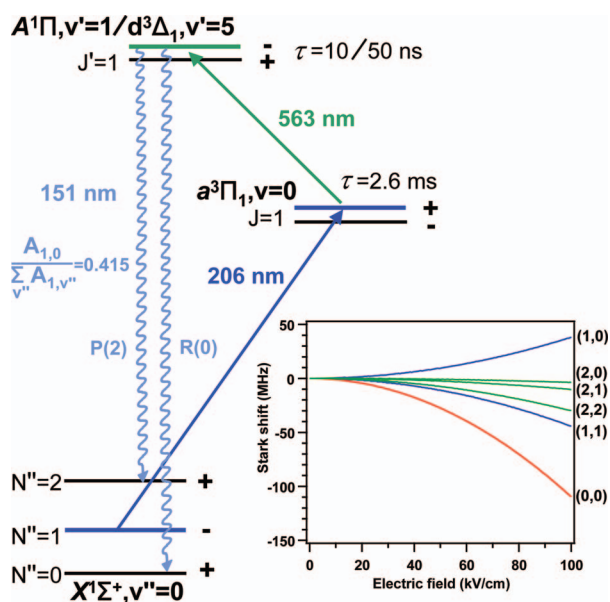


FIG. 1. Relevant energy levels of $^{12}\text{C}^{16}\text{O}$ involved in the unidirectional optical transfer demonstrated here. CO molecules are prepared in the $a^3\Pi_1, v=0$ metastable state by laser excitation from the electronic ground state. The metastable CO molecules can be slowed down to low velocities using a Stark decelerator and can then be optically pumped to the $J'=1$ level in the short-lived $A^1\Pi, v'=1/d^3\Delta_1, v'=5$ state. Up to 28% of the molecules in the metastable state can thus be transferred to the absolute ground level $X^1\Sigma^+, v''=0, N''=0$. The inset shows the Stark shifts for the lowest three rotational levels of ground-state $^{12}\text{C}^{16}\text{O}$ (labelled as $(N'', |M''|)$).

trap has been demonstrated^{12,13} and carefully characterized¹⁴ before, from which it is concluded that an electric trap with a depth of tens of micro-Kelvin can be made for ground-state CO molecules.

In the following sections, we outline and demonstrate a scheme via which the required translationally cold samples of ground-state CO molecules can be produced.

II. OPTICAL PUMPING SCHEME

A high density of CO molecules is obtained in a pulsed beam, e.g., when a mixture of CO in a rare gas carrier is expanded through a pulsed valve from high pressure into vacuum. In such a beam, a large fraction of all the CO molecules will be in the $v''=0$ and $N''=0$ level of the electronic ground state. Even though the vapor pressure of CO allows the pulsed valve to be cooled to liquid nitrogen temperatures, the speed of the molecules in the beam will be several hundred m/s. Deceleration of the CO molecules can be performed very efficiently when the molecules are first transferred to the metastable $a^3\Pi$ state. Pulsed laser excitation around 206 nm is used in the expansion region of the molecular beam to saturate the spin-forbidden transition to the metastable state. Molecules in the $J=1$ level of the $a^3\Pi_1, v=0$ state can be decelerated to arbitrarily low velocities; this has actually been used in the first demonstrations of various types of Stark decelerators.^{15–18}

After the metastable CO molecules have been brought to a standstill, they can be dumped back to the $X^1\Sigma^+, v''=0, N''=0$ level via stimulated emission pumping, thus produc-

ing the required translationally cold ground-state molecules. Preferably, there should be dissipation in the process of returning to the ground state, such that the phase-space density can be increased by accumulating molecules from subsequent cycles.^{19–22} Although the phosphorescence back to the electronic ground state could in principle be exploited for this, its millisecond time scale makes this impractical. It is shown here that it is possible to optically pump the CO molecules from the $a^3\Pi$ state to perturbed levels in the $A^1\Pi$ state, and to use the fast spontaneous emission on the $A^1\Pi \rightarrow X^1\Sigma^+$ transition to populate the ground-state level, as schematically shown in Fig. 1.

From the negative parity Λ -doublet component of the $J'=1$ level in the $A^1\Pi$ state, emission can only take place on R(0) and P(2) transitions, populating the $N''=0$ and $N''=2$ levels in various vibrational levels of the electronic ground state, respectively. We note here that the molecules in the $N''=2$ levels will be more difficult to trap because of their smaller Stark shift. In spite of the five-fold degeneracy of the $N''=2$ levels, the R(0) transitions are twice as strong as the P(2) transitions.²³ The total fraction of the spontaneous emission from the $A^1\Pi, v'=1$ level that ends up in the $X^1\Sigma^+, v''=0$ level, given by the ratio $A_{1,0}/\sum_{v''} A_{1,v''}$ of Einstein-A coefficients, is 0.415. This value is computed using the Rydberg-Klein-Rees (RKR) potentials and the high-level *ab initio* $A \leftarrow X$ transition dipole function described in Ref. 6. Therefore, if the excitation laser that drives the $A^1\Pi, v'=1, J'=1 \leftarrow a^3\Pi_1, v=0, J=1$ transition is intense enough and is on for a time that is long compared to the ~ 10 ns radiative lifetime of the $A^1\Pi$ state,²⁴ up to 28% of all the CO molecules in the $J=1$ level of the $a^3\Pi_1$ state can be transferred to the single $v''=0, N''=0$ level in the electronic ground state in this way. This transfer efficiency only holds when the parity of all the levels involved in the scheme is well defined. In an electric field the presence of states with mixed parity will result in leakage to the $N''=1$ level, decreasing the number of molecules ending up in the $N''=0$ level.

The success of this scheme depends on the strength of the spin-forbidden $A^1\Pi, v'=1 \leftarrow a^3\Pi, v=0$ transition. With the RKR potentials and *ab initio* spin-orbit couplings from Ref. 6, a value of 7.6×10^{-4} D is computed for the intrinsic transition dipole moment.²⁵ However, the $A^1\Pi$ state has numerous perturbations, for instance resulting from interactions with the $a'^3\Sigma^+, d^3\Delta$, and $e^3\Sigma^-$ states, which give significant triplet character to selected rotational and vibrational levels of the $A^1\Pi$ state. In $^{12}\text{C}^{16}\text{O}$, the low rotational levels of the $A^1\Pi, v'=1$ state, in particular, are perturbed by those of the $d^3\Delta_1, v'=5$ state, giving the $A^1\Pi, v'=1, J'=1$ level 17% $^3\Delta_1$ character.²⁶ Using *a-* and *d-*state RKR potentials based on Refs. 6 and 27 and a newly computed *ab initio* *d-a* transition dipole function,²⁵ a transition dipole moment of 0.17 D is calculated for the $d^3\Delta, v'=5 \leftarrow a^3\Pi, v=0$ transition. Therefore, the perturbation by the $d^3\Delta_1$ state makes the $A^1\Pi, v'=1, J'=1 \leftarrow a^3\Pi, v=0, J=1$ transition weakly allowed and considerably stronger than expected based on its intrinsic transition dipole moment.

To quantify the strength of this particular rotational transition further, we have to consider the Hönl-London factors

for the transitions from the $a^3\Pi_1$, $v = 0$, $J = 1$ level to the various rotational levels in the $d^3\Delta$, $v' = 5$ state. Unfortunately, the transitions with $\Delta\Omega = 0$ are forbidden in first order approximation; transitions from the $a^3\Pi_1$ spin-orbit manifold are strongest when they end up in the $d^3\Delta_2$ spin-orbit manifold, but this does not couple to the $A^1\Pi$ state. Using the available spectroscopic data for the $a^3\Pi$ state²⁷ and the $d^3\Delta$ state,²⁸ the transitions to the $J' = 1$ and $J' = 2$ levels in the $d^3\Delta_1$, $v' = 5$ state are calculated to have a Hönl-London factor of only 1.0×10^{-2} and 7.5×10^{-2} (when the sum of all transitions from the $J = 1$ level is normalized to $2J + 1 = 3$), respectively. Nevertheless, all together this still leads to an Einstein B-coefficient for the $d^3\Delta_1$, $v' = 5$, $J' = 1 \leftarrow a^3\Pi$, $v = 0$, $J = 1$ transition that is, for instance, about an order of magnitude larger than that for the $Q_2(1)$ transition in the Cameron band that is used to prepare the CO molecules in the $a^3\Pi_1$, $v = 0$, $J = 1$ level. This implies that the optical pumping of CO molecules from the metastable state to their absolute ground state via the $J' = 1$ level in the mixed $d^3\Delta_1$, $v' = 5 // A^1\Pi$, $v' = 1$ system can be induced by a continuous wave (cw) laser operating around 563 nm.

The existence of such “doorway” states in CO, via which transitions from the singlet manifold to the triplet manifold can be efficiently induced, has been known for a long time. In the early seventies already, emission from the mixed $d^3\Delta_1$, $v' = 5 // A^1\Pi$, $v' = 1$ system to excited vibrational levels of the $a^3\Pi$ state was observed in the visible part of the spectrum after vacuum ultra-violet (VUV) excitation from the ground state.²⁹ Perturbations of higher vibrational levels of the $A^1\Pi$ state with the $a^3\Sigma^+$ state have also been used to populate levels in the metastable triplet state via stimulated emission pumping.³⁰ The $A^1\Pi$, $v' = 1$, $J' = 1, 2 \leftarrow a^3\Pi$, $v = 0$, $J = 1$ and $d^3\Delta_1$, $v' = 5$, $J' = 1, 2 \leftarrow a^3\Pi$, $v = 0$, $J = 1$ rotational transitions around 563 nm have been observed both via depletion of metastable CO signal³¹ and via recording of the VUV emission to the ground state. Using the latter method, we have determined the lifetime of the excited states and the Stark shift of the aforementioned transitions, from which the degree of parity mixing in any electric field can be calculated.

III. EXPERIMENTAL

A pulsed beam of $^{12}\text{C}^{16}\text{O}$ molecules with a mean velocity of around 430 m/s is produced by expanding a mixture of 20% CO in xenon from a valve at room temperature. The CO molecules are excited to the upper Λ -doublet component of the $a^3\Pi_1$, $v = 0$, $J = 1$ level by direct laser excitation from the electronic ground state on the $Q_2(1)$ transition (indicated by the blue arrow in Fig. 1). The metastable CO molecules pass through a Stark decelerator with 108 electric field stages, described in more detail in Ref. 32. In the present study, the decelerator is operated in the $s = 3$ overtone guiding mode, producing a state-selected beam of metastable CO molecules with a mean velocity of 430 m/s. After exiting the decelerator the CO molecules are excited from the $a^3\Pi_1$ state to the lowest rotational levels in the $d^3\Delta_1$, $v' = 5$ and $A^1\Pi$, $v' = 1$ states, using either a pulsed or cw dye laser system, crossing the molecular beam under right angles. The pulsed laser

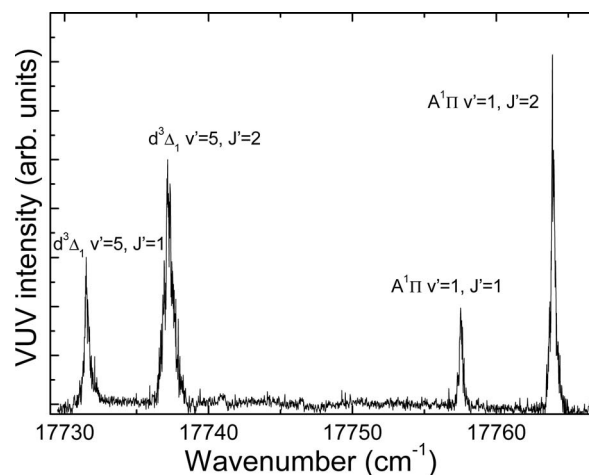


FIG. 2. VUV excitation spectrum of metastable $^{12}\text{C}^{16}\text{O}$ molecules. Using a pulsed laser, the molecules are optically excited from the upper (positive parity) Λ -doublet component of the $a^3\Pi_1$, $v = 0$, $J = 1$ level to the levels indicated in the figure, while the intensity of the VUV fluorescence back to the ground-state is recorded.

(5 ns pulse duration) is used to record an overview VUV spectrum and to determine the fluorescence decay times while the narrow-band cw ring dye laser system enables a high resolution measurement of the spectral line profiles, in particular of the Stark-splitting of the rotational transitions when an external electric field is applied. The cw ring dye laser is stabilized to a frequency-stabilized HeNe laser, resulting in an overall frequency resolution of 1 MHz, which is over an order of magnitude smaller than the spectral width of the peaks caused by residual Doppler and lifetime broadening. The transmission fringes of an etalon (free spectral range of about 150 MHz) are measured simultaneously to determine the relative frequency. The VUV emission from the $d^3\Delta_1$, $v' = 5$ and the $A^1\Pi$, $v' = 1$ states to the ground state is measured using a solar blind photomultiplier tube (Electron Tubes type 9424B), placed further downstream on the molecular beam axis. A homogeneous electric field, with a direction perpendicular to both the molecular beam axis and the laser beam propagation direction, can be applied in the detection region. For this, a voltage difference is applied to two circular electrodes (40 mm diameter) that are placed 6.9 mm apart.

An overview of the VUV excitation spectrum is shown in Fig. 2. The four lines observed in the spectrum end up in the lowest two rotational levels of the mutually interacting $d^3\Delta_1$, $v' = 5 // A^1\Pi$, $v' = 1$ states. The transitions are saturated and power-broadened, and the excitation spectrum shown here merely serves the purpose of identifying the various spectral lines. As discussed before, the intrinsic strengths of the transitions to the $J' = 1, 2$ rotational levels in the $d^3\Delta_1$, $v' = 5$ state are about a factor of five stronger than the corresponding transitions to the $A^1\Pi$, $v' = 1$ state and transitions to the $J' = 2$ levels are about a factor 7.5 stronger than those to the $J' = 1$ levels. In order of increasing frequency, the four transitions from the $a^3\Pi_1$, $v = 0$, $J = 1$ level thus have relative line strengths of 1.0:7.5:0.2:1.5.

In Fig. 3, the VUV fluorescence intensity is shown as a function of time during and after pulsed 563 nm laser

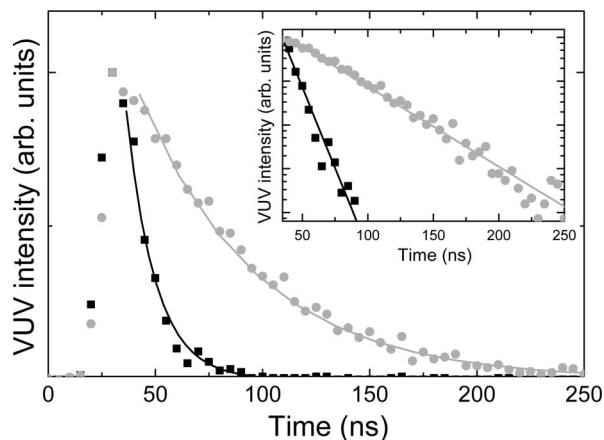


FIG. 3. VUV fluorescence intensity as a function of time for CO molecules laser excited to the negative parity component of the $A^1\Pi$, $v' = 1$, $J' = 1$ level (squares) and the $d^3\Delta_1$, $v' = 5$, $J' = 1$ level (dots). The solid curves result from a least-squares fit to singly exponentially decaying transients. In the inset, the tails of the VUV fluorescence data are shown on a logarithmic scale, together with the best fitting straight lines.

excitation to the $J' = 1$ levels of the $A^1\Pi$, $v' = 1$ state (squares) and the $d^3\Delta_1$, $v' = 5$ state (dots). The radiative lifetimes are extracted from the exponentially decaying tail of the VUV intensity after the laser excitation pulse is over. A weighed least-squares fit to a single exponentially decaying curve in the time interval from 35 to 90 ns gives a value of 13.5 ± 2.0 ns for the $A^1\Pi$, $v' = 1$, $J' = 1$ level. As the data acquisition system only has a time resolution of 5 ns and as the laser intensity will not drop off abruptly at the end of the pulse, this value is an upper limit for the radiative lifetime of the $A^1\Pi$, $v' = 1$, $J' = 1$ level. A similar fit in the time interval from 35 to 325 ns gives a radiative lifetime of 55 ± 4 ns for the $d^3\Delta_1$, $v' = 1$, $J' = 1$ level. As the radiative lifetime of unperturbed vibrational levels in the $d^3\Delta_1$ state is on the order of several micro-seconds³³ and thus much longer than that of the unperturbed $A^1\Pi$, $v' = 1$ state, the latter, τ_A , can be determined as the product of the two independently measured lifetimes divided by their sum, resulting in a value of $\tau_A = 10.8 \pm 1.8$ ns. Within the error bar, this value agrees with the deperturbed value of the radiative lifetime of the $A^1\Pi$ $v' = 1$ state as determined in the classic paper of Field *et al.*²⁴ The ratio of the two independently measured lifetimes is found as 4.1 ± 0.7 , and is a direct measure for the fraction of $A^1\Pi$ state over $d^3\Delta_1$ state character in the wavefunction of the $A^1\Pi$, $v' = 1$ state. The latter is actually known with high precision from spectroscopic data as 4.88,²⁶ and these independent lifetime measurements are thus seen to be consistent with this.

To determine the electric dipole moment of the $d^3\Delta_1$, $v' = 5$ state, we have recorded the shifts and splittings of the transition to the $J' = 1$ level in the presence of an external electric field. The high-resolution Stark-shift spectra of the $d^3\Delta_1$, $v' = 5$, $J' = 1 \leftarrow a^3\Pi_1$, $v = 0$, $J = 1$ transition are shown in Fig. 4 in electric fields up to 1.14 kV/cm for the excitation light polarized perpendicular (black curves) or parallel (grey curves) to the applied electric field. The Stark shifts are given relative to the frequency of the field-free transition at 17731.7 cm^{-1} .^{26,27} In the metastable $a^3\Pi_1$, $v = 0$ state only

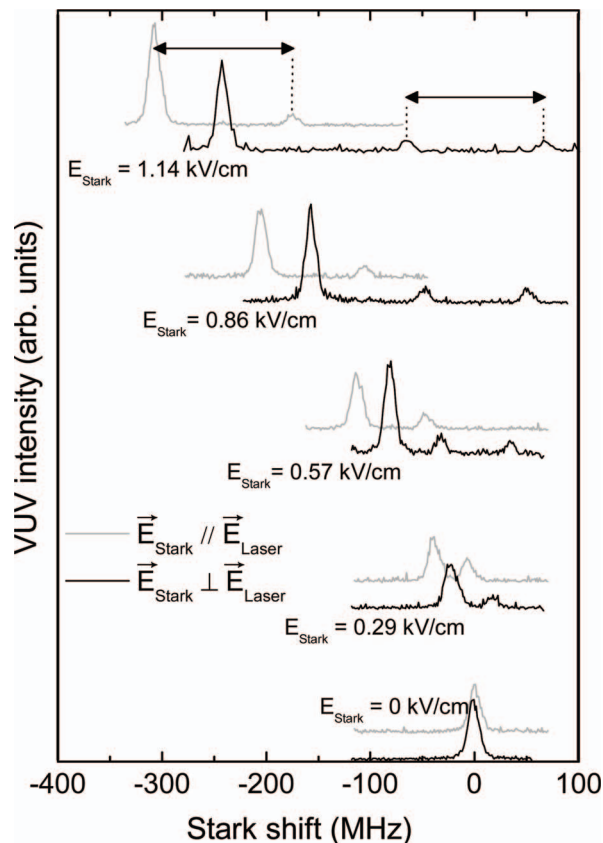


FIG. 4. Spectrum of the $d^3\Delta_1$, $v' = 5$, $J' = 1 \leftarrow a^3\Pi_1$, $v = 0$, $J = 1$ transition measured in electric fields up to 1.14 kV/cm. The black (grey) curves correspond to the situation where the light is polarized perpendicular (parallel) to the electric field.

the upper Λ -doublet component of the $J = 1$ level is populated. Although only molecules in the low-field seeking $M\Omega = -1$ component are actively guided through the decelerator, a minor fraction of metastable CO molecules might be present in the $M = 0$ level in the interaction region as well. In $^{12}\text{C}^{16}\text{O}$ these levels are degenerate in zero electric field, and transitions from the low-field seeking component to the $M = 0$ level are difficult to avoid in regions of low electric field,³⁴ e.g., near the exit of the decelerator.

When the polarization of the laser (\vec{E}_{Laser}) is perpendicular to the direction of the electric field (\vec{E}_{Stark}), the selection rule for the optical transitions is given by $\Delta M = \pm 1$. In this case, we expect a single strong transition originating from the low-field seeking $M\Omega = -1$ component in the metastable $a^3\Pi$ state to the $M = 0$ level(s) in the $d^3\Delta_1$ state. In the $d^3\Delta_1$ state, the Λ -doubling is expected to be negligibly small, and the two $M = 0$ levels (one of either parity) will thus be (nearly) degenerate. Furthermore, as these $M = 0$ levels will not shift at all in the relatively low electric fields that we have used in our experiments, the downward Stark shift of the strong transition as observed in Fig. 4 can be solely attributed to the upward Stark shift of the $M\Omega = -1$ component of the $a^3\Pi_1$, $v = 0$, $J = 1$ level. The latter is very well known, and the observed shift of this transition in the spectrum has, therefore, actually been used to accurately calibrate the applied electric fields, yielding the values given in the figure. The two additional weak peaks that are observed in the

spectrum for $\vec{E}_{\text{Laser}} \perp \vec{E}_{\text{Stark}}$ are the transitions from the $M = 0$ level in the $a^3\Pi$ state to the $M\Omega = \pm 1$ levels in the $d^3\Delta$ state. The splitting between these peaks, indicated by the solid arrow in the spectrum recorded in an electric field of 1.14 kV/cm, is given by $(\mu_{\Delta} E_{\text{Stark}})/h$, where μ_{Δ} is the magnitude of the electric dipole moment in the $d^3\Delta_1, v' = 5$ state, E_{Stark} is the magnitude of the applied electric field and h is Planck's constant.

The same splitting is also observed, and indicated as such, when the polarization of the laser is parallel to the electric field. In this case, the selection rule for the optical transitions is $\Delta M = 0$; transitions between $M = 0$ levels are forbidden. The two peaks that are observed in the spectrum both originate from the low-field seeking $M\Omega = -1$ component in the metastable $a^3\Pi$ state and go to the $M\Omega = \pm 1$ levels in the $d^3\Delta$ state. The magnitude of the observed splitting only gives information on the magnitude of the dipole moment but from the relative intensity of the two peaks information on the sign of the dipole moment can be extracted. As mentioned before, the transition from the $a^3\Pi$ state to the $d^3\Delta_1$ state is forbidden in first order approximation. It borrows transition dipole moment from the $\Delta\Omega = +1$ transitions via the weak intramolecular interaction between rotational levels with different quantum number Ω . In the presence of an electric field, it borrows additional transition dipole moment due to the Stark interaction between different J levels in both the $a^3\Pi$ and $d^3\Delta$ state; the observed electric field dependence of the (relative) intensity of the two peaks actually indicates that the latter effect is quite strong. The interference between the various contributions to the transition dipole moment can be constructive or destructive, depending on the mutual sign of the permanent electric dipole moment of the $a^3\Pi$ and $d^3\Delta$ state. The observed intensity ratio of the two peaks, and the way in which this ratio changes with increasing electric field, can only be quantitatively explained if the electric dipole moment in the $d^3\Delta, v' = 5$ state has a different sign than the dipole moment in the $a^3\Pi$ state. From the complete analysis of the spectra shown in Fig. 4, we thus deduce a value for the electric dipole moment in the $J'' = 1$ level of the $d^3\Delta_1, v' = 5$ state of $-(0.23 \pm 0.01)$ D.

The electric dipole moment of CO in the $v' = 3, v' = 4$, and $v' = 6$ levels of the $d^3\Delta$ state has been determined earlier as -0.48 D, -0.42 D, and -0.28 D, respectively.³⁵ From a linear interpolation of these values, one would have expected a value of around -0.35 D for the dipole moment in the $v' = 5$ level. Due to the perturbation with the $A^1\Pi, v' = 1$ state, however, this value is slightly reduced, as will be discussed in more detail later.

To determine the electric dipole moment of the $A^1\Pi, v' = 1$ state, we have recorded the shifts and splittings of the transition to the $J' = 2$ level in the presence of an external electric field; the transition to the $J' = 1$ level that we would have preferred to use is unfortunately too weak for this. The high-resolution Stark-shift spectra of the $A^1\Pi, v' = 1, J' = 2 \leftarrow a^3\Pi_1, v = 0, J = 1$ transition are shown in Fig. 5 in electric fields up to 1.14 kV/cm for the excitation light polarized perpendicular (black curves) or parallel (grey curves) to the applied electric field. The Stark shifts are given relative to the frequency of the field-free transition at 17763.9 cm^{-1} .^{26,27} In

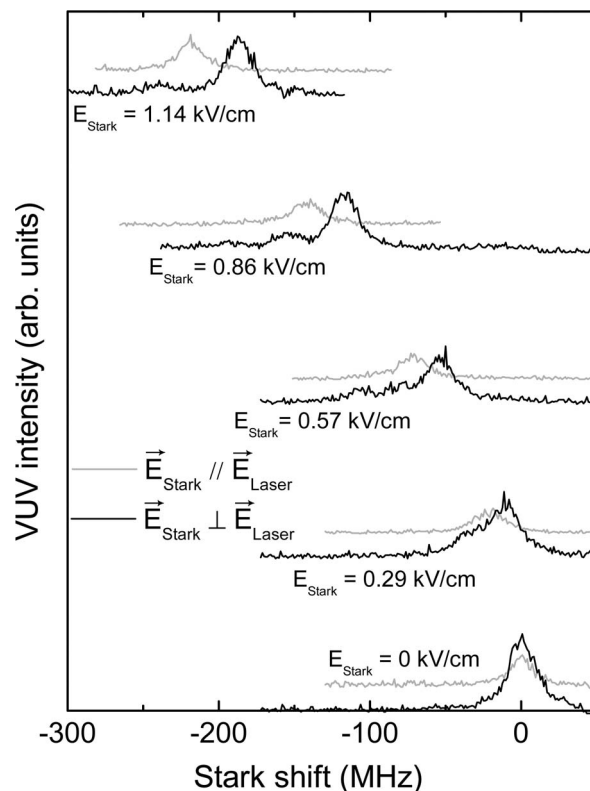


FIG. 5. Spectrum of the $A^1\Pi, v' = 1, J' = 2 \leftarrow a^3\Pi_1, v = 0, J = 1$ transition measured in electric fields up to 1.14 kV/cm. The black (grey) curves correspond to the situation where the light is polarized perpendicular (parallel) to the electric field.

these experiments, only the low-field seeking $M\Omega = -1$ component of the $J = 1$ level in the $a^3\Pi_1, v = 0$ state appeared to be significantly populated.

For the $A^1\Pi$ state, it is not expected that the Λ -doubling can be neglected and the magnitudes of both the Λ -doubling and the dipole moment need to be extracted from the observed Stark shifts. The observed shifting of the transitions to lower frequency with increasing electric field is again mainly due to the increase in Stark energy of the level in the $a^3\Pi$ state. The least shifted component is observed when $\vec{E}_{\text{Laser}} \perp \vec{E}_{\text{Stark}}$, i.e., when $\Delta M = \pm 1$ such that the most upward shifting $M\Omega = -2$ component in the $A^1\Pi$ state can be reached. The shoulder at slightly larger redshift is due to the transition to the $M = 0$ component. When the polarization of the laser is parallel to the direction of the electric field, the $M\Omega = -1$ component can be reached, and this transition is indeed seen to be spectrally located in between the two transitions just mentioned. It turns out that in this case the observed intensities can not only be used to determine the sign of the dipole moment but also to unambiguously establish that the upper (lower) Λ -doublet component of the $J' = 2$ level in the $A^1\Pi, v' = 1$ state has negative (positive) parity. Only in this case the observed intensity pattern is quantitatively reproduced and, in particular, the factor two intensity difference in the strength of the transition to the $M\Omega = -2$ component compared to the transition to the $M\Omega = -1$ component is obtained. From a fit of the observed Stark shifted patterns, a value of the Λ -doublet splitting between the parity levels under field-free conditions

of 18 ± 3 MHz is obtained. The electric dipole moment in the $J' = 2$ level of the $A^1\Pi$, $v' = 1$ state is determined to be $+(0.29 \pm 0.02)$ D.

IV. CONCLUSIONS

In this paper, we have outlined and demonstrated an experimental scheme to produce samples of translationally cold CO molecules in their absolute ground-state level. The scheme is based on the use of the remarkably efficient unidirectional optical transfer from the metastable $a^3\Pi$ state to the $N' = 0$ level in the $X^1\Sigma^+$, $v'' = 0$ state *via* the $J' = 1$ level in the perturbed $d^3\Delta_1$, $v' = 5 // A^1\Pi$, $v' = 1$ system. The radiative lifetime of the $J' = 1$ level in the (nominally) $d^3\Delta_1$, $v' = 5$ state is indeed seen to be as short as 55 ± 4 ns due to the coupling with the singlet state. Fluorescence from this rotational level in the triplet manifold will end up in the singlet manifold, in particular in the $X^1\Sigma^+$ electronic ground state, with a quantum efficiency that is very close to unity (about 0.99). The transition to this level from the metastable state can be efficiently induced by a cw laser; in the present experiments about 300 mW of narrowband 563 nm laser radiation in a 2 mm diameter beam has been used to drive this transition.

As the manipulation of the translational motion of the metastable CO molecules relies on their interaction with electric fields, it is important to know the dipole moments of the intermediate levels in the optical transfer scheme as well. The dipole moment of the $J' = 1$ level in the $d^3\Delta_1$, $v' = 5$ state is found to be $-(0.23 \pm 0.01)$ D. The dipole moment in the perturbing $A^1\Pi$, $v' = 1$ state has the opposite sign; for the $J' = 2$ level it is found to be $+(0.29 \pm 0.02)$ D. From a detailed analysis of the perturbation between these states, it is known that the amount of $^1\Pi$ character in the wavefunction of the $d^3\Delta_1$, $v' = 5$, $J' = 1$ level is 17% whereas in the wavefunction of the $J' = 2$ level in the $A^1\Pi$, $v' = 1$ state it is 84.3%.²⁶ The deperturbed value of the dipole moment of the $d^3\Delta$, $v' = 5$ state can then be calculated as $-(0.36 \pm 0.02)$ D, whereas the deperturbed value for the $A^1\Pi$, $v' = 1$ state results in $+(0.41 \pm 0.03)$ D. The first value falls nicely in between the values found for the adjacent (unperturbed) vibrational levels of the $d^3\Delta$ state.³⁵ The deperturbed value of the dipole moment for the $v' = 1$ level in the $A^1\Pi$ state is somewhat higher than the value of $+(0.335 \pm 0.013)$ D that has been found for the $v' = 0$ level.³⁶ A slight increase of the permanent electric dipole moment with increasing vibrational quantum number is indeed expected from the calculated dipole moment function for the $A^1\Pi$ state.³⁷

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