Production of an intense pulsed beam of oriented metastable CO a $^3\Pi$

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CO molecules in a supersonic molecular beam are resonantly excited from the X $^1\Sigma^+$, $v''=0$ ground state to the a $^3\Pi$, $v'=0$ metastable state using pulsed laser radiation at 206 nm. In the excitation region a static electric field is applied to split individual M components of a given rotational line of this electronic transition. The splitting can be made larger than the Fourier-limited bandwidth of the pulsed radiation source and specific M levels in the a $^3\Pi$ state can be populated. Peak fluxes of 10^{17} (10^{15}) oriented CO a $^3\Pi_1$, $v'=0$, $J'=1$, $M'=1$ (a $^3\Pi_2$, $v'=0$, $J'=2$, $M'=2$) molecules per second are obtained.

For many years there has been a great interest in producing molecular beams of oriented molecules for the study of steric effects in reactive molecular scattering and orientation effects in molecule–surface interactions [1,2]. Two main techniques are used for the production of these beams. In the first technique electric hexapole fields are used to focus molecules in a specific $|JKM\rangle$ level, while molecules in other $|JKM\rangle$ levels are blocked or deflected out of the beam [3,4]. Here J is the total rotational angular momentum with projections K and M on the molecular symmetry axis and on the laboratory-fixed direction of the electric field, respectively. This technique is applicable to effective symmetric top molecules which have a first-order Stark effect and it requires a relatively large molecular beam apparatus. In the second method, called the brute-force technique, strong static electric fields are used to physically twist polar molecules in low J states into orientation. Very cold beams of highly polar molecules with small B constants are needed. This latter technique has recently been developed by Loesch and

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Remscheid [5] in Bielefeld and, independently, by Friedrich and Herschbach [6] in Harvard and can be used even for diatomic Σ state molecules possessing an electric dipole. A disadvantage of the latter technique is that the average orientation that can be obtained is relatively small.

Here we describe a technique for the production of an intense pulsed beam of fully state-selected and oriented electronically excited molecules. A pulsed laser with a Fourier-limited bandwidth is used to induce an electronic transition to a metastable state that has a largely different Stark splitting from the electronic ground state. In a static electric field the individual M components of a specific $J'\leftarrow J''$ transition are split far enough apart that a single $|J', K', M'\rangle$ level in the metastable state can be populated with a pulsed laser. This technique has the simplicity of the brute-force method, but no brute-force field strengths are required.

It should be noted that vibrationally excited molecules have been produced in a similar way [7–9]. Because the dipole moment of the vibrationally excited state and the vibrationless state are usually very similar, higher electric fields are needed to sufficiently split the M components. Narrow bandwidth cw lasers are then used to populate specific

$|J', K', M'\rangle$ levels in the vibrationally excited state. Sufficient excitation efficiency is only obtained when the Stark transition of the molecule under investigation can be tuned into resonance with an intense fixed frequency IR laser.

We produced a pulsed beam of oriented CO (a $^3\Pi$) by pumping jet-cooled CO via the spin-forbidden a $^3\Pi$, $v'=0\leftarrow X\ ^1\Sigma^+$, $v''=0$ transition (Cameron band) at 206 nm. The $^1\Sigma^+$ electronic ground state of CO has no first order Stark splitting and with a relatively small electric dipole moment of 0.10 D the splitting of the various M levels is of the order of a few MHz in electric fields of up to 4 kV/cm. The lowest energy electronically excited state of CO is the metastable a $^3\Pi$ state which *does* show a first-order Stark splitting. The CO molecules in the a $^3\Pi$ state have an electric dipole moment of 1.37 D, enough to cause M-level splittings of several GHz in the forementioned fields [10]. Individual M components of rotational lines of the spin-forbidden a $^3\Pi$, $v'=0$ $\leftarrow X\ ^1\Sigma^+$, $v''=0$ transition will therefore be separated by several GHz in easily obtainable electric fields. Fully state-selected and oriented metastable CO molecules can then be produced by excitation on a single M component in the CO Cameron band. A radiation source with a high spectral brightness is required for an efficient excitation of M component resolved rotational lines in the weak Cameron transition. The spin-forbidden a $^3\Pi \leftarrow X\ ^1\Sigma^+$ transition becomes weakly allowed because the A $^1\Pi$ state interacts with the a $^3\Pi$ state. This interaction gives oscillator strength to transitions to the a $^3\Pi$ $\Omega=1$ multiplet only. For low J values the a $^3\Pi_1$ multiplet can therefore be reached much more easily than the other multiplets. The individual rotational levels in the a $^3\Pi$, $v'=0$ state of CO have radiative lifetimes of several ms [11], long enough to perform molecular beam experiments. An advantage of using CO is that neither the C atom nor the O atom have a nuclear spin which would couple to the total angular momentum and destroy the orientation of the molecules at low electric fields.

The a $^3\Pi$ state of CO is best described as an intermediate case between Hund's case (a) and (b). For low values of J, the total angular momentum vector, the three different Ω multiplets ($\Omega=0$, 1, 2), Ω being the sum of the projection of the electron spin and the electron angular momentum on the inter-

nuclear C–O axis, are only weakly interacting and can be treated separately. The first-order Stark effect is proportional to $M\Omega$, and therefore only the $\Omega=1$ and $\Omega=2$ multiplets will show an appreciable Stark splitting. In fig. 1 the Stark splitting for the $J=1$ level in the a $^3\Pi_1$ multiplet is schematically indicated. At zero electric field the two Λ-doublet components with opposite parity are split by 394 MHz [10]. If an electric field is applied the M degeneracy is lifted and parity is no longer a good quantum number thus levels with different parity start to mix. There is no interaction between $M=0$ states with different parity, however. In the high field limit four separate levels corresponding to $M\Omega=+1$ (up-shifted), $M\Omega=-1$ (down-shifted) and the two unaffected $M=0$ levels are seen. Due to the relatively large Λ-doublet splitting in a $^3\Pi_1$, $J'=1$ the mixing of + and – parity levels is not complete at the applied electric fields. At the maximum applied field of 4 kV/cm the upshifted (down-shifted) level consists of 99.5% of $M\Omega=-1$ (+1) character and of 0.5% of $M\Omega=+1$ (-1) character.

The angular probability distribution of the CO axis for a specific $|J\Omega M\rangle$ level, indicated by $P_{J\Omega M}(\Theta)$ d cos Θ where Θ is the angle between the molecular axis and the electric field vector, is a function of the product $M\Omega$. The mean orientation for CO in an electric field is given by

$$\langle \cos \Theta \rangle = \left[1 + \left(\frac{E_\Lambda}{2E_{\text{Stark}}} \right)^2 \right]^{-1/2} \frac{M\Omega}{J(J+1)},$$

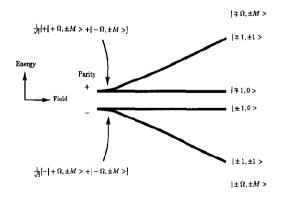where E_Λ is the Λ-doublet splitting and E_{Stark} is the

Fig. 1. Schematic view of Stark splitting in a $^3\Pi_1$, $v'=0$, $J'=1$ as a function of the applied electric field.

Stark shift given by $E_{Stark} = \mu_{el}EM\Omega/J(J+1)$. For CO (a $^3\Pi$) a maximum average orientation of $\frac{1}{2}$ and $\frac{2}{3}$ can be reached for a $^3\Pi_1$, $J'=1$, $M'=1$ and a $^3\Pi_2$, $J'=2$, $M'=2$, respectively. Due to the Λ doublet splitting the mean average orientation at the maximum applied field of 4 kV/cm is 0.49 and 0.66 respectively, very close to the high-field limit. The angular probability distribution in this limit is proportional to $P_{111}(\Theta)$ d cos $\Theta \sim (1+\cos\Theta)^2$ and $P_{222}(\Theta)$ d cos $\Theta \sim (1+\cos\Theta)^4$.

The experiment is carried out with a molecular beam of CO, formed by expanding a 10:1 He:CO mixture at 2.5 atm stagnation pressure through a pulsed valve with an orifice of 1 mm. During operation the background pressure in the vacuum chamber is below 10^{-5} Torr. Two 40 mm diameter brass electrodes spaced 20 mm apart are used to apply an electric field of up to 4 kV/cm perpendicular to the molecular beam axis, a few centimeter downstream from the beam orifice. A 4 mm diameter laser beam crosses the molecular beam between the electrodes, some 50 mm away from the nozzle. Here the jet-cooled CO X $^1\Sigma^+$, $v''=0$ molecules are resonantly excited to the a $^3\Pi$, $v'=0$ state by the radiation of a home-built pulsed dye amplifier (PDA) system. Narrow bandwidth radiation (0.5 MHz) from a cw ring dye laser (Spectra Physics 380D) operating on DCM dye seeds the PDA system, which is pumped by a frequency-doubled Nd:YAG (Quantel) laser. The output of the PDA is frequency doubled in a KDP crystal and the frequency-doubled and fundamental beam are then mixed in a BBO crystal to produce radiation at 206 nm with an energy of 1 mJ per pulse and a Fourier-limited bandwidth of 290 MHz. The polarization vector of the laser beam makes an angle ϕ with the electric field vector of the applied Stark field. Most times ϕ is set close to the magic angle ϕ_m of 54.7° [12] such that the transition strengths to separate M levels of a given J level are all equal. The excited metastable CO molecules have 6.0 eV internal energy and a radiative lifetime of several milliseconds. The metastable CO molecules collide onto the cathode of a particle multiplier, and are detected via the electrons that are created in the direct Auger de-excitation process [13]. The particle multiplier is placed about 15 cm downstream from the excitation region to diminish the effects of residual Doppler broadening in the molec-

ular beam on the observed spectral linewidth. The signal from the particle multiplier is processed by a digital oscilloscope (LeCroy 9400) and a boxcar integrator (SRS 250) interfaced with a PDP 11/23 computer. Neither fluorescence nor ionization were observed, which suggests that the CO a $^3\Pi$ molecules are not excited to still higher electronic states by absorption of additional photons.

In fig. 2 the measured rotational transition from X $^1\Sigma^+$, $v''=0$, $J''=0$ to a $^3\Pi_1$, $v'=0$, $J'=1$ (the $R_2(0)$
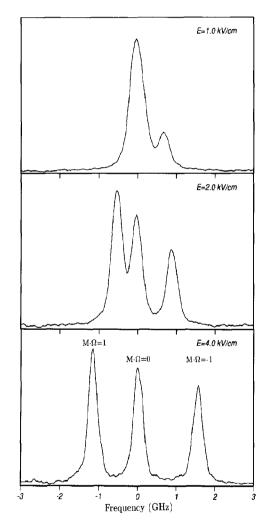

Fig. 2. Observed splitting of the $R_2(0)$ transition of CO around 48478.48 cm^{-1} as a function of the electric field in the excitation region. The polarization vector of the excitation laser is chosen such that all ΔM transitions appear equally strong. Due to the fact that $M=0$ states with different parity do not interact, only the transition to the $M=0$ state with parity is observed.

transition [14] around 48478.48 cm^{-1}) is shown in different electric fields. At the maximum applied field of 4 kV/cm three components corresponding to $M\Omega = +1, 0$ and -1 are completely separated. When the polarization vector of the laser beam is set parallel or perpendicular to the direction of the applied electric field, only the $\Delta M = 0$ or the $\Delta M = \pm 1$ transitions are observed, respectively, as expected. The parity of the $J'' = 0$ level in the electronic ground state of CO is positive, and therefore only levels with negative parity in the a $^3\Pi_1$ multiplet can be reached. From the observed splitting pattern it can be concluded unambiguously that the lowest Λ-doublet component of a $^3\Pi_1$, $v' = 0$, $J' = 1$ has negative parity, in agreement with the results found in ref. [10].

Although the transition moment for the $R_3(1)$ transition is a factor 50 smaller than for the $R_2(0)$ transition, it is still very well possible to excite to a $^3\Pi_2$, $v' = 0$, $J' = 2$ via the $R_3(1)$ transition as shown in fig. 3. The outermost two peaks of the observed quintet are due to CO a $^3\Pi$ molecules with an average orientation of $\langle \cos \Theta \rangle = \frac{2}{3}$.

Unfortunately, it is not possible to determine the absolute number of oriented CO a $^3\Pi$ molecules from the measured signals because the detection efficiency of the metastables depends strongly on the workfunction, and thereby the cleanliness, of the cathode of the particle multiplier. The number of excited molecules can be calculated using the measured laser intensity, the estimated density of CO molecules in the molecular beam, and the calculated absorption cross section for the a $^3\Pi \leftarrow X ^1\Sigma^+$ transition. James [11] calculated the lifetime for individual rotational levels in the a $^3\Pi$, $v' = 0$ state and from these calculated lifetimes absorption cross sections for the $R_2(0)$ and $R_3(1)$ transitions of 7.2×10^{-20} cm^2 cm^{-1} and of 1.3×10^{-21} cm^2 cm^{-1} are estimated, respectively. The laser fluence at the excitation zone is 3.3×10^{15} photon/cm^2 whereas the CO density at the excitation zone is estimated to be 1.2×10^{15} molecule/cm^3. Due to rotational cooling 50% of the CO molecules are in the $J'' = 0$ level of the vibrational and electronic ground state while roughly 40% are in the $J'' = 1$ level. The number of molecules excited to one specific M sublevel of the a $^3\Pi_1$, $v' = 0$, $J' = 1$ state is estimated to be 5×10^{11}. For the excitation to the a $^3\Pi_2$, $v' = 0$, $J' = 2$ level this number is a factor 200 lower. The laser interacts with the CO molecules over
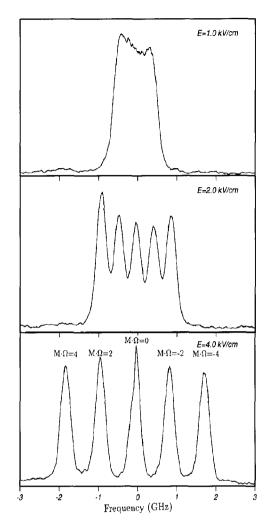

Fig. 3. Observed $R_3(1)$ transition of CO as a function of the electric field in the excitation region, again with an angle between the polarization vector of the laser and the applied electric field close to the magic angle of 54.7°.

a length of 4 mm, corresponding to a time interval of 3 μs, taking 1300 m/s as the velocity for molecules in the molecular beam. The peak flux of oriented molecules is then 2×10^{17} molecule/s for a $^3\Pi_1$, $J' = 1$ and 1×10^{15} molecule/s for a $^3\Pi_2$, $J' = 2$. This peak flux is orders of magnitude higher than the fluxes reported up to now for hexapole oriented beams, and this flux can still be increased by focusing of the 206 nm radiation.

In conclusion, a technique to produce an intense pulsed beam of state-selected and oriented metastable CO molecules is presented. CO molecules in

a supersonic molecular beam are resonantly excited from the $X\,^1\Sigma^+$, $v''=0$ ground state to the a $^3\Pi$, $v'=0$ metastable state using pulsed laser radiation of 206 nm. In the excitation region a static electric field of a few kV/cm is applied, enough to split individual M components of a given rotational line of this electronic transition by several GHz. This splitting is larger than the Fourier-limited bandwidth of the pulsed radiation source and specific M levels in the a $^3\Pi$ state can be populated. Fluxes of over 10^{11} oriented CO a $^3\Pi_1$, $v'=0$, $J'=1$, $M'=1$ molecules per microsecond are obtained.

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