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Polarizability of CO_2 studied in molecular-beam laser Stark spectroscopy

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The polarizability of the CO_2 molecule in excited vibrational states has been studied using molecular-beam laser Stark spectroscopy techniques. The analysis yields the polarizability anisotropies $\Delta\alpha = 2.215(7)$ Å^3 for the 00°1 state, 2.244(7) Å^3 for the 02°0 state, and the difference of the isotropic polarizabilities $(\alpha_{00^\circ 1} - \alpha_{02^\circ 0}) = -0.0124(8)$ Å^3.

I. INTRODUCTION

The average static polarizability (α) of a molecule[1,2] in the gas phase at normal laboratory temperatures can be measured accurately by determining the dielectric constant of the gas.[3,4] Microwave interferometry has been used to determine the index of refraction of the gas, and hence the polarizability at low frequencies.[5] Optical measurements of the index of refraction are also useful in determining the frequency dependence of the polarizability.[6] All above techniques measure the average value of the polarizability. The polarizability anisotropy, which is related to the orientation of the molecule with respect to an external field, may be investigated by measuring the depolarization ratio for Rayleigh scattering[7] and via the quadratic Stark effect.[8]

CO_2 is a polyatomic molecule which does not exhibit a permanent dipole moment and, therefore, is better suited than polar molecules for second-order Stark effect measurements since in polar molecules the effects caused by the permanent electric dipole moment tend to dominate. The CO_2 molecule is also a good candidate for the study of the vibrational contributions to α, since in the case of homonuclear diatomic molecules, the vibrational contributions to α vanish in view of their zero vibrational transition dipoles.[2] Therefore CO_2 offers a very good opportunity for examining the relative magnitudes of the electronic and vibrational contributions to the static polarizability α.

For linear or symmetric-top molecules only the diagonal elements of the polarizability tensor are nonzero. The polarizability may be separated into parallel and perpendicular parts with respect to the molecular axis: $\alpha_\parallel = \alpha_{zz}$ and $\alpha_\perp = \alpha_{xx} = \alpha_{yy}$. Two quantities, referred to as the isotropic part (α) and anisotropic part ($\Delta\alpha$) of the polarizability, can be defined in terms of $\alpha_\parallel$ and $\alpha_\perp$: $\alpha = (\alpha_\parallel + 2\alpha_\perp)/3$ and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$.

The isotropic part of the static polarizability of CO_2 was determined by dielectric constant and microwave refractive-index measurements,[9,10] which gave $\alpha = 2.913(2)$ Å^3. The electronic contribution, α^{el}, to α was determined by extrapolation of optical dispersion data to zero frequency:[11] $\alpha^{\text{el}} = 2.595(1)$ Å^3. As will be discussed later, the difference between α and α^{el} agrees with the vibrational contribution α^{vib} predicted from infrared-intensity data.

Stark spectroscopy of CO_2 in a molecular beam has been carried out on the rovibrational transitions of the "$\nu_1 + \nu_3$" band in this laboratory by Gough, Orr, and Scoles using a color center laser.[12] The polarizability anisotropies associated with both ground and vibrationally excited states were determined to be 2.60 and 2.65 Å^3, respectively. The limited body of Rayleigh depolarization ratio dispersion data for CO_2 suggest that the electronic contribution to $\Delta\alpha$ is given by[7] $\Delta\alpha^{\text{el}} = 2.05(1)$ Å^3. The difference between $\Delta\alpha$ and $\Delta\alpha^{\text{el}}$ deviates from the vibrational contribution $\Delta\alpha^{\text{vib}}$. This discrepancy as well as the lack of complete information on the vibrational dependence of the polarizability invite more experimental and theoretical work.

The anisotropy of the molecular polarizability, in addition to its intrinsic interest, is important in the evaluation of molecular quadrupole moments[13] and the magnetic susceptibility anisotropies.[14] It is also relevant to the evaluation of the anisotropy of long-range intermolecular forces. The frequency dependence of $\Delta\alpha$ may be used to deduce the orientation dependence of the long-range dispersion coefficients.[15]

In this paper, quadratic Stark spectroscopy of one of the two main CO_2 lasing transitions is studied using two CO_2 lasers and a beam of vibrationally excited CO_2 molecules. From the spectroscopic data the polarizability anisotropies of the 02°0 and 00°1 vibrationally excited states are determined with high accuracy.

II. THEORETICAL BACKGROUND

The application of an external electric field F to a molecule results in a perturbation which shifts the energy levels and causes splittings of the spectral lines arising from the transitions between these levels.

For the CO_2 molecule in a vibrational state v, the energy levels in a uniform electric field F may be expressed as

$$\begin{aligned} E_{v,JKM} &= hcB_v J(J+1) + \langle JM \mid H_\alpha \mid JM \rangle \\ &= hcB_v J(J+1) - \tfrac{1}{2}\alpha_v F^2 \\ &\quad - \Delta\alpha_v F^2 \frac{J(J+1)/3 - M^2}{(2J+3)(2J-1)} , \end{aligned} \tag{1}$$

where B_v is the rotational constant and J,M are rotational quantum numbers. Equation (1) shows that the Stark effect for CO$_2$ is quadratic in F, and that the energy levels for different values of $|M|$ are split by an amount which depends on $\Delta\alpha_v F^2$. By the measurement of different Stark components, $\Delta\alpha_v$ for a certain vibrational level may be obtained. The isotropic part α_v may be measured by comparing the Stark spectra with the rovibrational spectra obtained in the absence of a Stark field.

As an example consider the shift and the splitting of the $R(2)$ rovibrational transition. In the presence of an electric field, the upper energy level ($J=3$, $v=00^\circ1$) splits into four sublevels and the lower ($J=2$, $v=-02^\circ0$) into three sublevels; thus $R(2)$ splits into eight transitions as shown in Fig. 1.

The relationship between the polarizability tensor and the transition dipole moment may be readily obtained as[2]

$$\alpha_{ij}^{(n)}=\frac{2}{h}\sum_k \frac{\omega_{nk}}{\omega_{nk}^2-\omega^2}\langle n\,|\mu_i|\,k\rangle\langle k\,|\mu_j|\,n\rangle\ . \tag{2}$$

The summation over k may be broken into two parts: the sum over vibrational states not belonging to the ground electronic state, and, the sum over vibrational states in the ground electronic state. Normally, the CO$_2$ molecule is in the ground electronic state. If $|nv\rangle$ represents a molecule in the electronic state n and vibrational state v, Eq. (2) may be written as

$$\alpha_{ij}^{(0v)}=\frac{2}{h}\sum_m\sum_u \frac{\omega_{ov-mu}}{\omega_{ov-mu}^2-\omega^2}\times\langle 0v\,|\mu_i|\,mu\rangle\langle mu\,|\mu_j|\,0v\rangle+\frac{2}{h}\sum_u\frac{\omega_{vu}}{\omega_{vu}^2-\omega^2}\langle 0v\,|\mu_i|\,0u\rangle\langle 0u\,|\mu_j|\,0v\rangle\ . \tag{3}$$

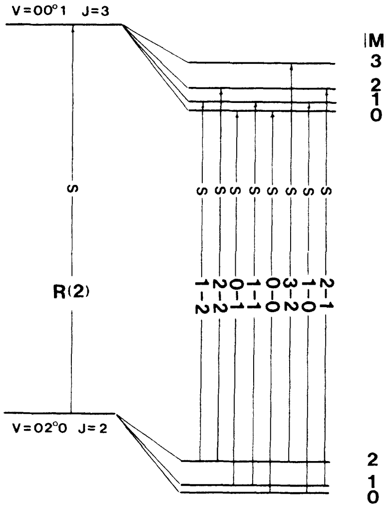


FIG. 1. Energy-level scheme for the rovibrational Stark spectra of the $R(2)$ transition in the 9.4-μm band of CO$_2$.

The first term obviously represents the electronic contributions to the polarizability tensor and may be measured in the visible and ultraviolet regions. The second term contains the vibrational contributions and may be determined from infrared-intensity data.

The static polarizability represents the limiting case for $\omega\to0$, that is,

$$\alpha_{ov}(0)=\lim_{\omega\to0}\alpha_{0v}(\omega)=\alpha_0^{\text{el}}(0)+\alpha_v^{\text{vib}}(0)\ . \tag{4}$$

As may be seen in the above equations the vibrational contributions are negligible for $\omega\gg\omega_{0v}$, but not when $\omega\to0$,

$$\alpha_{v,ij}^{\text{vib}}=\frac{2}{h}\sum_u\frac{1}{\omega_{vn}}\langle v\,|\mu_i|\,u\rangle\langle u\,|\mu_j|\,v\rangle\ . \tag{5}$$

The matrix elements $\langle v\,|\mu|\,u\rangle$ may be evaluated from infrared-intensity data:[12]

$$|\langle v\,|\mu_{(z\text{ or }x)}|\,u\rangle|^2=\frac{3hc}{8\pi^3}(F_{vu}g_u\omega_{vu})^{-1}S_{vu}\ , \tag{6}$$

where F_{vu} is a factor determined by the vibrational partition function, a Boltzmann population difference factor, and g_u the degeneracy of state u. The S_{vu} term is the line strength, i.e., the integrated absorption coefficient of the vibrational band ($v\to u$).

The combination of Eqs. (5) and (6) yields

$$\alpha_{v,\parallel\text{ or }\perp}=\frac{3}{4\pi^3}\sum_{u(\neq v)}F_{vu}g_u^{-1}\omega_{vu}^{-2}S_{vu(\parallel\text{ or }\perp)}\ . \tag{7}$$

The polarizability thus calculated may be compared with the results obtained from spectroscopic Stark measurements.

III. EXPERIMENTAL DETAILS

The laser molecular-beam spectrometer used in this experiment consists of a supersonic molecular-beam source, an interaction region with Stark plates, and a bolometer detector which responds to a modulated energy input into the beam caused by chopping or frequency modulating the laser illumination.

A schematic diagram of the experimental apparatus is shown in Fig. 2. The molecular beam was formed by expanding a mixture of 25% CO$_2$ in He gas under a source pressure of 7 atm. A quartz nozzle of 30 μm diameter was located 1.5 cm from a skimmer of 0.5 mm diameter. A tungsten coil and a stainless-steel reflector around the nozzle can heat the source temperature up to 1400 K. A liquid-He-cooled germanium bolometer (Infrared Laboratories, Inc.) detects the absorption signal of the molecules with a responsivity of 4.2×10^5 V/W and a noise-equivalent power (NEP) of 4.2×10^{-14} W/$\sqrt{\text{Hz}}$ at 80 Hz.

The laser power used was 0.54W with equal horizontal and vertical polarization. Three $\Delta M=0$ transitions (see Fig. 3) were identified using two polarizer/attenuators (II-IV, Inc.) to allow only the vertically polarized light (parallel to the direction of the Stark field) to interact with the molecular beam. The other four transitions are, obviously, due to $\Delta M=\pm1$ transitions.

Since only the separations between the different Stark

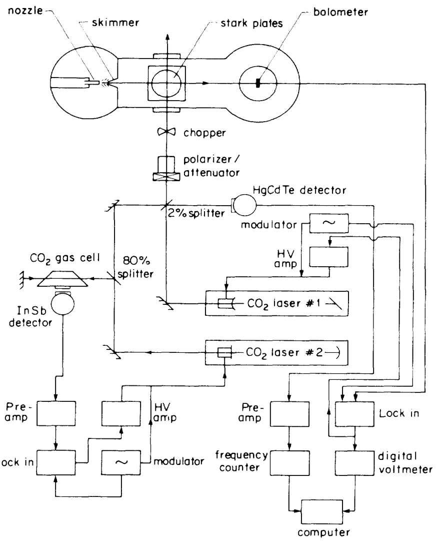


FIG. 2. Experimental apparatus for the CO_2 laser stabilization and heterodyne-frequency measurement.

components, rather than their absolute frequencies, are important, a heterodyne frequency measurement was chosen for this experiment. As shown in Fig. 2, CO_2 laser 1 was stabilized using the 4.3-μm fluorescence Lamb dip technique[16] providing in this way for a frequency "standard." CO_2 laser 2 was instead stabilized using any one of the molecular-beam absorption transitions.[17] The two laser beams were then combined with a beam splitter and were superimposed at a Hg-Cd-Te detector (Model MPV11-0.1-B50, New England research). The beat signal was fed into a preamplifier (Model 115, Princeton Applied Research) and sent to a frequency counter (Model 5316A, Hewlett-Packard). A computer was used for data acquisition, recording simultaneously the data from the frequency counter and the absorption signal from the bolometer. By subsequently stabilizing the laser 2 using each of the beam transitions an entire frequency-calibrated spectrum could be obtained.

The Stark electrodes were made of a pair of polished stainless-steel circular plates of 5 cm diameter. The electrodes were installed in such a way that the electric field was vertical, perpendicular to the horizontal molecular and laser beams. The spacing of the Stark electrodes was calibrated by means of the known Stark spectrum for the ν_2 band of NH_3, excited by the CO_2 laser. The resonant Stark fields, with the relative accuracy of 10^{-4}, were reported in Ref. 18. The calibration yields an electrode spacing of 0.7147(9) mm and a Stark field of 205.3(3) kV/cm for this experiment. The voltages were read from a high-voltage power supply (Model 205A-30P, Bertan Associates, Inc.) which was calibrated at the National Research Council Standards Laboratory in Ottawa with an accuracy of 0.025%.

IV. RESULTS AND DISCUSSION

The Stark spectrum of the $R(2)$ transition was obtained by cavity tuning CO_2 laser 2 piezoelectrically and recording the absorption signal from the bolometer at the same time. Figure 3 shows seven Stark components out of the eight calculated components under the Stark field of 205.3(3) kV/cm. The frequency of the missing component $|M| = 1 \leftarrow 2$ (about 26 MHz from the center of Doppler profile) is beyond the tuning range of the CO_2 laser.

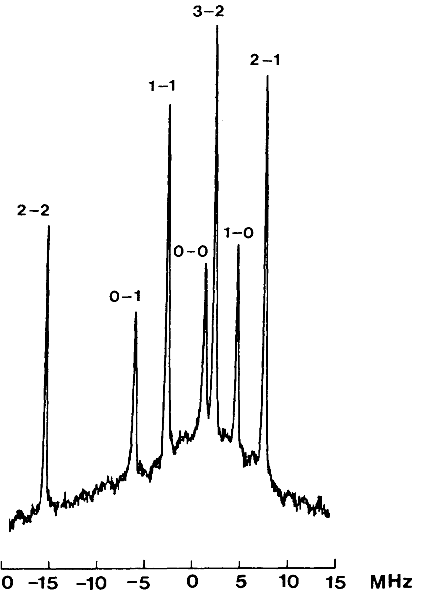


FIG. 3. Stark spectra of the $R(2)$ transition of CO_2. Seven peaks are labeled with respect to the value of $|M|$ in upper and lower states. The broad background is due to scattering of the laser beam into the bolometer.

For the Stark spectra of the $R(2)$ transition, the assignment of the different M values involved is relatively simple. From Eq. (1), the frequencies of three parallel components may be calculated and it is interesting to note they are related by an integer, $(f_{1\text{-}1} - f_{2\text{-}2})/(f_{0\text{-}0} - f_{1\text{-}1}) = 3$. Using this relationship and the calculated intensities, three parallel components were easily assigned as in Fig. 3. The perpendicular components were assigned using the parallel components as frequency markers and the calculated intensities.

Having assigned all the transitions, their frequencies were measured by the heterodyne technique. While the "tunable" laser was stabilized onto the center of each Stark component, the beat frequencies were recorded with a gate time of 70 ms. Two hundred beat frequency values were averaged for each measurement. The results for the seven transitions are listed in Table I, in which the zero frequency is taken to be the frequency of the $R(2)$ rovibrational transition in the absence of a Stark field.

The accuracy of the frequency measurements can be assessed by the frequency relationship $(f_{1\text{-}1} - f_{2\text{-}2})/(f_{0\text{-}0} - f_{1\text{-}1}) = 2.995$, which differs by only 0.17% from the integer 3. The full width at half maximum of each Stark component is about 200 kHz at the laser power of $0.27W$.

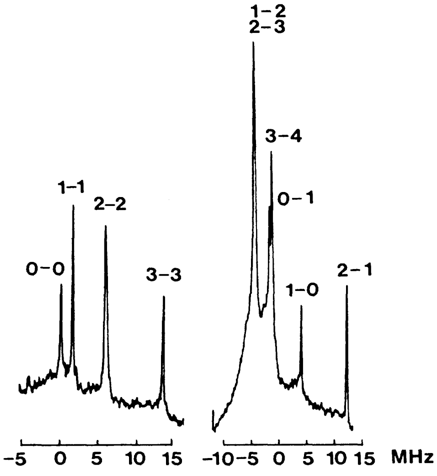
The parallel and perpendicular Stark spectra of the

TABLE I. Stark spectroscopic results for the $R(2)$ transition of CO_2.

Upper level $\|M\|$	Lower level $\|M\|$	Measured frequency (MHz)	Calculated frequency (MHz)
2	1	8.13±0.09	8.07
1	0	5.25±0.10	5.16
3	2	2.80±0.09	2.76
0	0	1.73±0.08	1.65
1	1	−2.41±0.10	−2.47
0	1	−6.02±0.10	−5.98
2	2	−14.81±0.09	−14.81

$P(4)$ transition of CO_2 are shown in Figs. 4(a) and (b), respectively, at the Stark field of 205.3(3) kV/cm. The frequencies are listed in Table II. Among them the components (2-3) and (1-2), (3-4) and (0-1) are not well resolved.

One interesting phenomenon observed in this experiment is that there is no absorption signal in the beam in the 10.4-μm band, i.e., involving excitations of the CO_2 molecule from the 10^00 to the 00^01 state. This phenomenon is explained by the coupling of the 10^00 and 02^00 states and the strong rotational cooling present in the beam. Since the two lower laser states 10^00 and 02^00 are very close (102.8 cm^{-1} apart), a strong perturbation (Fermi resonance) causes a mixing of the eigenfunctions of the two states. This perturbation originates from the anharmonic terms in the potential energy expression. On the other hand, because of the very low rotational temperature, only a few low J levels are populated. The mixing of the two states moves the molecules from the 10^00 state to the higher J levels of 02^00 state, then the cooling effect further causes them to drop down. This process "drains" the molecules out from the 10^00 state. These results would seem to indicate that resonant rovibrational energy transfer is as fast if not faster than the relaxation of the rotational states. The original plan of measuring the polarizability of the 10^00 state was not accomplished. However, on the positive side, this process populates the 02^00 state and therefore increases the S/N ratio for the experiment.



(a) (b)

FIG. 4. Stark spectra of the $P(4)$ transition of CO_2: (a) recorded with only parallel components and (b) recorded with only perpendicular components.

TABLE II. Stark spectroscopic results for the $P(4)$ transition of CO_2.

Upper level $\|M\|$	Lower level $\|M\|$	Measured frequency (MHz)	Calculated frequency (MHz)
3	3	13.13±0.10	13.15
2	2	5.90±0.09	5.99
1	1	1.57±0.08	1.69
0	0	−0.09±0.04	0.26
2	1	12.23±0.08	12.23
1	0	3.70±0.09	3.77
3	4	−1.68±0.07	−1.40
0	1		−1.82
1	2	−4.60±0.07	−4.55
2	3		−4.41

The two sets of data in Tables I and II were fitted using a linear least-square routine. The fitting function is based on Eq. (1) and has the form

$$y(i)=A+Bx(i)+Ch(i) , \tag{8}$$

where $y(i)$ is the measured frequency divided by F^2, $x(i)$ is determined by the quantum numbers in the upper state, and $h(i)$, those in the lower state. The fitted parameters A, B, and C stand for $-\frac{1}{2}(\alpha_{001}-\alpha_{020})$, $\Delta\alpha_{001}$, and $\Delta\alpha_{020}$, respectively. The fitting gives $(\alpha_{001}-\alpha_{020}) = -0.0124(8)$ Å^3, $\Delta\alpha_{001}=2.215(7)$ Å^3, and $\Delta\alpha_{020}=2.244(7)$ Å^3, respectively. Among the eight observed Stark components in the $P(4)$ spectrum, the (3-4),(0-1), and (2-3),(1-2) transitions were not included in the fit since they are unresolved; neither was the (0-0) component because of its large error in frequency measurement. These values can be used in Eq. (1) to calculate the Stark spectra; the results are listed in the last volumes of Tables I and II.

The errors reported above are those from the fitting routine. It should be stressed that the α's measured from the Stark effect are the static polarizabilities, which, as we will see, are different from the molecular optical polarizabilities $\alpha(\omega)$. In the following we will evaluate the electronic and vibrational contributions to the polarizability.

The frequency-dependent polarizability anisotropy of CO_2 has been measured from the depolarization ratio for Rayleigh scattering in the visible region.[7,19] The resulting values of $\Delta\alpha(\omega)$ at three discrete frequencies are given below:

ω	6.143	5.827	4.738	10^{14} Hz
$\Delta\alpha(\omega)$	2.155	2.140	2.112	Å^3
$\alpha(\omega)$	2.665	2.658	2.636	Å^3

where the isotropic part of the polarizability $\alpha(\omega)$ was obtained by an evaluation of literature data by Bogaard

TABLE III. Vibrational contributions to the polarizability calculated from infrared-intensity data.

State v	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\Delta\alpha$	α
00°0	0.468	0.257	0.211	0.327
02°0	0.506	0.264	0.242	0.345
00°1	0.460	0.260	0.200	0.327

TABLE IV. A comparison between the vibrational contributions to the polarizability $\Delta\alpha^{\text{vib}}$(IR) and $\Delta\alpha^{\text{vib}}$(S-R).

	$\Delta\alpha_{020}^{\text{vib}}$	$\Delta_{001}^{\text{vib}}$	$\alpha_{020}^{\text{vib}}-\alpha_{001}^{\text{vib}}$
(IR)	0.242	0.200	0.018
(S-R)	0.19(1)	0.17(1)	0.0124(8)

et al.[7] Both $\Delta\alpha$ and α become smaller as the frequency decreases. By extrapolation of the $\Delta\alpha(\omega)$ and $\alpha(\omega)$ values to zero frequency, we obtain the electronic contribution to the polarizability α^{el} and $\Delta\alpha^{\text{el}}$. Fitting these data to the equation

$$\Delta\alpha(\omega)=\frac{\Delta\alpha(0)}{1-\text{const}\times\omega^2}\ , \tag{9}$$

we obtain $\Delta\alpha^{\text{el}}=2.05(1)$ Å^3 and $\alpha^{\text{el}}=2.595(1)$ Å^3.

The vibrational contribution to the polarizability can be predicted from the infrared intensity data as Eq. (7) suggested. Braun and Rebane[20] have tabulated the band centers and the intensities for the 560 bands of the CO_2 molecule. The calculated α^{vib} for the ground vibrational and two excited states are summarized in Table III. The details of the calculation are presented in Ref. 21.

Comparison can now be made between the vibrational contributions to the polarizability, calculated from infrared intensity data [$\Delta\alpha^{\text{vib}}$(IR)], and the vibrational contributions, calculated as the difference between our total static values and the electronic contribution measured by Rayleigh scattering data extrapolated to zero frequency [$\Delta\alpha^{\text{vib}}$(S-R)]. The results are shown in Table IV.

The differences between $\Delta\alpha^{\text{vib}}$(IR) and $\Delta\alpha^{\text{vib}}$(S-R) for the 02°0 and 00°1 states are about 20% and arise probably because of the diversity of the infrared intensity data used in the calculations.

V. CONCLUSION AND OUTLOOK

This paper reports the study of the polarizability of the CO_2 molecule by means of laser Stark spectroscopy in a molecular beam. Several conclusions may be drawn from the results.

(i) The static polarizability anisotropies of the 02°0 and 00°1 vibrational states have been measured to an accuracy of $\sim$0.5%. The difference between the isotropic part of these two states has also been measured, although with lesser accuracy ($\sim$6%).

(ii) The polarizabilities measured for the individual vibrational states clearly show a vibrational dependence. The magnitude of the change is $\sim$1–2%. The calculations from the infrared intensity data confirm this dependence.

(iii) Using the heterodyne technique, with two frequency stabilized CO_2 lasers, a high resolution and accuracy in the Stark spectrum has been achieved with a relatively simple experimental setup. The FWHM of the Stark components is about 200 kHz and the center of the absorption may be determined, under optimal conditions, to within a few kHz.

The successful application of laser Stark spectroscopy techniques to a molecular beam of CO_2 shows that other nondipolar molecules, such as SF_6, SiH_4, SiF_4, and GeH_4 may be studied in the future.

Another interesting application of our study is the possible orientation of the angular momentum of the CO_2 molecule in the beam. In the Stark spectrum of $R(2)$, for example, the $|M|=3\leftarrow2$ transition orients the angular momentum parallel to the Stark field and, the $|M|=0\leftarrow0$ and $|M|=0\leftarrow1$ transitions orient the angular momentum perpendicular to the Stark field. Thus the CO_2 molecules in the beam are not only prepared in a known electronic, vibrational and rotational state, but also with a certain orientation. This may have potential applications in the study of state-to-state chemical reaction, molecule-surface interactions, and so on.

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