High resolution pulsed-cw double-resonance spectroscopy on the B $^1\Sigma^+$($v' = 0$) ← A$^1\Pi$($v'' = 0$) system of CO

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Abstract

A 2 + 1 double-resonance laser-induced fluorescence technique is described in which the high power of a pulsed laser is combined with the narrow bandwidth of a single-mode cw ring dye laser. The combination of these laser systems allows the study of highly excited states with MHz resolution. This double-resonance technique has been applied to the study of the B $^1\Sigma^+$($v' = 0$) ← A$^1\Pi$($v'' = 0$) system of CO. From the high resolution spectra the term value of the A state could be determined, $T = 64748.0091 \pm 0.0019$ cm^{-1}, corresponding to an increased accuracy over previously reported values by an order of magnitude.

1. Introduction

The spectroscopy of highly excited states of molecules has been hampered in the past by the lack of intense and tunable light sources in the VUV and XUV region of the electromagnetic spectrum. With the rapid development of laser technology during the last decades it is nowadays possible to generate tunable coherent VUV and XUV radiation via third-order frequency conversion in atomic or molecular gases for the study of these states. Because of the high powers required for the generation of intense VUV radiation pulsed lasers are used and consequently the resolution is limited to typically 0.1 cm^{-1}.

A technique that allows the study of high-lying electronically excited states at high resolution, is double-resonance spectroscopy. This has been elegantly demonstrated by Meijer et al. [1,2] who studied the E $^2\Sigma^+$($v = 0$) state of NO at an energy of 65000 cm^{-1} with a resolution of several MHz. In that experiment the A$^2\Sigma^+$($v' = 0$) state of NO at an energy of about 44000 cm^{-1} was efficiently populated using a pulsed dye laser and in a next step a single-mode cw dye laser was employed to probe the high lying E state with MHz resolution.

In this Letter we report an extension of this technique. Instead of populating an intermediate state via a 1-photon transition we populate a high-lying intermediate state using a 2-photon transition that enables us to study states at even higher energies with MHz resolution. The experiments are performed on the B $^1\Sigma^+$($v' = 0$) ← A$^1\Pi$($v'' = 0$) system of CO. The A state, at an energy of 64750 cm^{-1}, is populated with a pulsed dye laser via a two-photon

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transition after which the B ← A transition is probed by a single-frequency ring dye laser.

The carbon monoxide molecule has been the subject of extensive spectroscopic studies for more than 100 years, see reference [3] for an overview. Despite these extensive studies the absolute energies of many electronic states in CO are only known with an accuracy ~ 0.1 cm^{-1}. The relative positions of many electronically excited states, however, have been determined well within a 0.01 cm^{-1} level by high resolution Fourier transform infrared (FTIR) spectroscopy [4–7] or infrared diode laser spectroscopy [8]. The A$^1\Pi$ state, the most prominent feature in the absorption spectrum of carbon monoxide, has not been investigated using these accurate infrared techniques. In 1985 Le Floch and Amiot [9] recorded the B ← A system by visible Fourier transform spectroscopy and could determine the relative position of these states with respect to each other within 0.02 cm^{-1}. The B state has been the subject of a recent high resolution laser induced fluorescence study [10] and the absolute position of the energy levels could be determined with a precision of 0.002 cm^{-1}. The high resolution spectra recorded in the present experiment can therefore be used to determine the absolute position of the energy levels of the A$^1\Pi(v = 0)$ state with the same high precision.

2. Experimental

The experiments are performed in the following way. A molecular jet of CO is formed by expanding neat CO through a pulsed valve with an orifice of 1 mm diameter. A laser beam that induces the 2-photon A$^1\Pi(v'' = 0)$ ← X$^1\Sigma(v'' = 0)$ transition crosses the jet 50 mm downstream of the nozzle. For this purpose a Nd:YAG (Continuum 681-10C) pumped dye laser (Continuum TDL 60) is employed. The dye laser is operated with DCM dye and its output is frequency doubled in a KDP crystal yielding 10 mJ of tunable light around 310 nm with a bandwidth of ~ 0.2 cm^{-1}. The doubled light is softly focussed ($f = 100$ cm) into the molecular jet to induce the 2-photon transition. The resulting VUV fluorescence from the A state down to the electronic ground state is monitored by a solar blind photomultiplier tube (EMI 9413) placed in the vacuum chamber at right

angles with both the molecular jet and the laser beam.

A single-mode cw ring dye laser (Spectra Physics 380D), operated with Stilbene 3 dye is used to induce the B$^1\Sigma^+(v' = 0)$ ← A$^1\Pi(v'' = 0)$ transition. The output power at 440 nm is typically 200 mW whereas the bandwidth is less than 1 MHZ. For absolute frequency calibration the absorption spectrum of the Te$_2$ molecule is recorded [11,12] along with the B$^1\Sigma^+(v' = 0)$ ← A$^1\Pi(v'' = 0)$ excitation spectrum. For relative frequency calibration the transmission fringes of a pressure and temperature stabilized Fabry-Perot interferometer with a free spectral range of 149.72 MHz are recorded. In order to excite molecules efficiently from the A state to the B state the counterpropagating cw laser beam is also focussed into the jet using an $f = 50$ cm lens. The fluorescence from the B state down to the various vibrational levels of the A state is collected by a quartz F/0.7 lens system and imaged onto a photomultiplier tube (EMI 9893B). To reduce the scattered light from both the cw and the pulsed laser a GG 475 cut-off filter is placed in front of this photomultiplier. The signals from both photomultipliers are processed by a digital oscilloscope (LeCroy 9400) and two boxcar integrators (SRS 250) interfaced with a personal computer.

3. Results

In a first step a rotational level in the A$^1\Pi(v'' = 0)$ state is populated by the frequency doubled pulsed dye laser. Fig. 1 shows a recording of the A$^1\Pi(v'' = 0)$ ← X$^1\Sigma(v'' = 0)$ 2-photon transition, detecting the
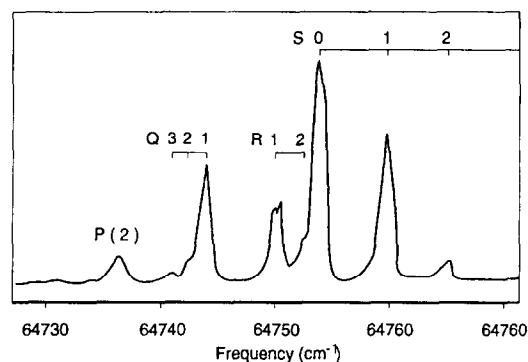

Fig. 1. Laser-induced fluorescence spectrum of the A$^1\Pi(v'' = 0)$ ← X$^1\Sigma(v'' = 0)$ two-photon transition in CO.

VUV fluorescence from the A state to the electronic ground state. Due to the low rotational temperature, 4 K, only the lowest three rotational levels are substantially populated and a relatively simple excitation spectrum is obtained. Besides P, Q and R transitions, O and S transitions characteristic of two-photon excitation, are also observed. According to the selection rules for a two-photon transition the e-parity Λ-doublet component in the A state is probed by $\Delta J = 0, \pm 2$ transitions, whereas the other Λ-doublet component, f-parity, is probed by $\Delta J = \pm 1$ transitions. These selection rules also prohibit observation of the R(0) transition.

A double resonance spectrum is obtained by keeping the pulsed laser fixed on a $A^1\Pi(v' = 0) \leftarrow X^1\Sigma(v'' = 0)$ transition while the cw laser is scanned over the wavelength region of the $B^1\Sigma^+(v' = 0) \leftarrow A^1\Pi(v'' = 0)$ system. From the selection rules for this $^1\Sigma^+ \leftarrow ^1\Pi$ system it follows that e-parity levels in the A state can only be probed by $\Delta J = \pm 1$ transitions, whereas f-parity can only be probed by $\Delta J = 0$ transitions. Fig. 2 shows the $B^1\Sigma^+(v' = 0) \leftarrow A^1\Pi(v'' = 0)$ P(2) transition after the $J = 2$ rotational level in the A state is populated via an S(0) transition. The linewidth of this P(2) transition amounts to 145 MHz and is determined mainly by the residual Doppler broadening in the molecular jet. The homogeneous line broadening caused by the relatively short lifetimes of both the A and the B states [10,13] is negligible.
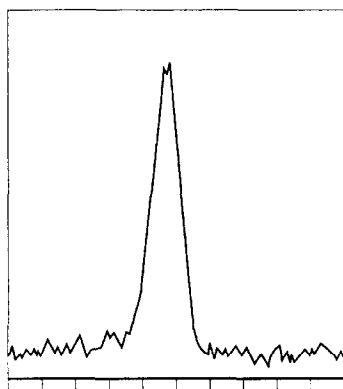

Fig. 2. Recording of the $B^1\Sigma^+(v' = 0) \leftarrow A^1\Pi(v'' = 0)$ P(2) double-resonance transition. The $J = 2$ level in the A state is populated via the $A^1\Pi(v'' = 0) \leftarrow X^1\Sigma(v'' = 0)$ S(0) transition. The frequency is marked every 150 MHz.

Table 1
Observed line positions (cm^{-1}) of the $B^1\Sigma^+$ ($v' = 0$) $\leftarrow$ $A^1\Pi(v''= 0)$ transition in carbon monoxide

Trans.	Frequency	Trans.	Frequency
P(1)	22168.171(2)	R(1)	22179.861(2)
P(2)	22165.670(2)	R(2)	22185.178(2)
P(3)	22163.943(2)	R(3)	22191.199(2)
P(4)	22162.921(2)	R(4)	22197.985(2)

The number of transitions that can be studied at high resolution is limited by the signal-to-noise ratio. Only the strongest $A \leftarrow X$ transitions provide a high enough population in the A state that a double-resonance signal can be observed. Therefore, most of the observed transitions involve the e-parity Λ-doublet components in the A state that can be populated using the strong S transitions. Only one $B \leftarrow A$ transition involving a f-parity Λ-doublet component in the A state is observed, i.e. the Q(2) transition. Unfortunately, the absolute frequency of this transition could not be accurately determined since the Te_2 absorption spectrum is sparse in this frequency region. The frequencies of the other observed $B \leftarrow A$ transitions are listed in Table 1. The error in the listed frequencies is mainly determined by the uncertainty at which the line center of a Te_2 absorption line can be determined.

4. Discussion

Since the first studies of the B state it is well known that the high rotational levels of this state are subjected to a strong predissociation [3]. Until recently it was assumed that no other perturbations are present in the B state. However, recent high resolution studies on the B state using Fourier transform spectroscopy [7] and two-photon laser-induced fluorescence spectroscopy [10] have revealed that this state is weakly perturbed at low J-levels by the nearby lying $e^3\Sigma^-(v = 28)$ state. The relative positions of the rotational energy levels determined in those studies are confirmed by the combination differences of the P and R transitions observed in the present experiment. Since the B state is so well characterized, the rotational energy levels of the A state can be calculated from the observed transition

frequencies. However, a correction of 0.008 cm^{-1} has to be applied to the reported absolute energy levels of the B state [10] due to a systematic error of the reported line positions in the Te$_2$ atlas used for absolute frequency calibration [11,12] of the B state. The calculated energies of the A state levels including this correction are given in Table 2.

The A$^1\Pi$ state of CO has been the subject of extensive studies. Although previous low resolution studies showed that the A state undergoes numerous perturbations the first comprehensive study of the A state was performed in 1972 by Field et al. [14]. They established the appropriate energy matrix and fitted all the absorption and emission data involving the A state and its perturbing states. This systematic analysis provided deperturbed band origins and rotational constants for the A state. Recently this perturbation analysis has been extended to rotational levels up to $J = 75$ by Le Floch et al. [15] The observed rotational structures were fitted to an effective Hamiltonian incorporating 10 perturbing states, yielding a matrix of dimension 26. Although the perturbing states cross the A state at relatively high rotational levels, $J > 10$, the low J-levels are also strongly perturbed due to the strong interaction strengths. The energy of the lowest rotational levels in the A state of CO can therefore not be described by the simple equation normally used to describe the rotational structure in $^1\Pi$ states. Since the spectra obtained by the low resolution work can be perfectly described by the Hamiltonian in Ref. [15] it can be expected that the parameters for this Hamiltonian are accurate enough to describe the spectra obtained in the present study, even though the resolution in the present experiment is an order of magnitude higher. In Table 2 the calculated energies of the lowest rotational levels are listed. When the calculated values are compared with the experimentally determined values, a J-independent difference of -0.037 cm^{-1} is observed. This difference is most probably caused by a difference in the absolute values of the transition frequencies determined in this and other experiments. It is well known that it is difficult to determine the absolute frequency of a transition better than 0.1 cm^{-1} by conventional grating spectroscopy. Since our spectra are calibrated to the Te$_2$ frequency standard, the values reported in this study are probably the most accurate ones. In order to describe the present results with the Hamiltonian of Ref. [15] the deperturbed term value of the A$^1\Pi(v = 0)$ state has to be changed to $T = 64748.0091 \pm 0.0019$ cm^{-1}. Our high resolution spectra can thus be described by the model of Le Floch et al. [15] and yield a more accurate value for the term value of the A state.

In the present experiment pulsed-cw double resonance spectroscopy is applied to obtain high precision constants for the intermediate A$^1\Pi(v = 0)$ state since the higher lying B$^1\Sigma^+(v = 0)$ state had already been studied at high resolution [10]. However, usually the intermediate state is better characterized than the higher lying state and this technique will thus be used to obtain accurate information on the higher lying state. The maximum energy of states that can be studied by this technique is determined by the energy of the intermediate state that can be populated with the present laser systems. Using β-BaB$_2$O$_4$ as a nonlinear material for frequency conversion of the pulsed laser, wavelengths down to 188 nm can be generated. In combination with a cw dye laser that operates in the visible and near UV range of the electromagnetic spectrum electronic, in principle, states at energies as high as 130000 cm^{-1} can be studied. The resolution at which this can be done is limited by the lifetimes of both the electronic states involved and by the residual Doppler broadening in the molecular beam. As has been shown by Meijer et al. [1,2] in the 1 + 1 pulsed-cw double-resonance study of NO, a resolution of the order of 10 MHz can be achieved when using a well collimated molecular beam.

5. Conclusion

A high resolution 2 + 1 pulsed-cw double-resonance technique is presented which allows, in princi-

Table 2
Observed and calculated [15] energies (cm^{-1}) of rotational levels of the A$^1\Pi(v'' = 0)$ state of CO

J	Parity	Observed	Calculated	Obs. − calc.
1	e	64747.986(2)	64748.025	−0.039
2	e	64754.357(2)	64754.394	−0.037
3	e	64763.904(2)	64763.940	−0.036
4	e	64776.614(2)	64776.651	−0.037

ple, the study of electronically excited states up to 130000 cm^{-1} with MHz resolution. This technique has been demonstrated on the B $^1\Sigma^+(v' = 0) \leftarrow$ A$^1\Pi(v'' = 0)$ system of CO. In a first step the A state has been populated by 2-photon excitation with a tunable pulsed laser after which the B $\leftarrow$ A transition has been probed by a narrow bandwidth cw ring dye laser. The observed transition frequencies have been used to derive accurate energy levels of the A state. These values have been compared with recent calculations based upon lower resolution spectra [15]. It has been found that a perfect agreement could be found when the term value for the A$^1\Pi(v = 0)$ state is corrected by -0.0037 cm^{-1}, giving $T = 64748.0091 \pm 0.0019$ cm^{-1}.

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