Doppler-free two-photon spectroscopy on the $S_1 \leftarrow S_0$ origin band of 1,4-diazabicyclo[2,2,2]octane (DABCO)

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Abstract

The rotationally resolved two-photon excitation spectrum of the Q-branch ($\Delta J = 0$) of the 0_0^0 band in the $S_1 \leftarrow S_0$ transition of DABCO was recorded in a cell at room temperature. Two counterpropagating narrow bandwidth laser beams were used for Doppler-free excitation. The observed linewidth was 20 MHz. Analysis of the spectra provides the change upon electronic excitation of the rotational constants.

1. Introduction

In the past, much attention has been paid to the assignment of the vibrationally resolved electronic spectra of 1,4-diazabicyclo[2,2,2]octane (DABCO, $C_6H_{12}N_2$) [1–4] and several Van der Waals clusters [5–7]. Knowledge of the structural changes of the DABCO monomer upon electronic excitation can clarify the analysis of those spectra. This information can be obtained from rotationally resolved electronic excitation spectra.

DABCO is a highly symmetric amine whose symmetry belongs to the D_{3h} point group. It does not possess a permanent dipole moment. Therefore no information on the ground state geometrical structure can be obtained by microwave spectroscopy. Transitions to vibrational levels in the S_1 state, which is totally symmetric, are one-photon forbidden and two-photon allowed (electric dipole transitions). Several forbidden vibrational transitions into the S_1 state are partially allowed through a coupling of the S_1 state with another excited state [1,2]. Consalvo et al. [4] reported the rotationally resolved one- and two-photon

laser-induced fluorescence (LIF) excitation spectra of several bands in the $S_1 (A_1') \leftarrow S_0(A_1')$ system of jet-cooled DABCO at a resolution of 400 MHz. The 0_0^0 band could be measured after two-photon excitation or one-photon excitation (quadrupole transition) and turned out to be a totally symmetric band of a symmetric top molecule (selection rules $\Delta K = 0$ and $\Delta J = 0$, ± 1, ± 2). Analysis of these spectra provided the rotational B constant in the ground state. The A constant could not be determined due to the selections rules of this band. Only an upper limit could be determined for the change in the rotational constants upon electronic excitation (ΔA and ΔB), because the changes are small and progressions in the K-quantum number were not observed due to the low rotational temperature and limited spectral resolution.

When linear polarized photons are used to induce a two-photon transition between totally symmetric states in a symmetric top molecule, the Q-branch transitions are dominant [8,9]. This has been observed in the 0_0^0 band of jet-cooled DABCO [4]. The low rotational temperature allowed the observation of rotational levels up to $J = 5$. The intensity of the unre-

solved Q-branch was three orders of magnitude larger than the intensity of the strongest rotational transition in the P-branch. Glownia et al. [10] reported a study of the potential of DABCO vapor for the amplification of resonantly tuned picosecond pulses by two-photon stimulated emission (TPSE). The electronic energy level structure of DABCO in combination with its high symmetry was thought to be favorable for TPSE. An important parameter in the design of a TPSE amplifier is the width of the two-photon spectrum. For DABCO this width is defined by the sharpness of the Q-branch and depends on the rotational substructure, which is determined by the values of ΔA and ΔB.

In the aforementioned rotational resolved study on DABCO [4], the resolution was limited by the Fourier transform of the temporal profile of the excitation laser. Better resolution can be achieved by using narrow bandwidth cw lasers. The combination of such lasers and strongly collimated supersonic molecular beam expansions have been shown to be a powerful tool in resolving the rotational structure of large molecules [11]. However, a two-photon experiment with such a system on DABCO would be difficult, due to the low density of DABCO molecules in the molecular beam, the low two-photon absorption probability and the low cw laser powers. In addition, low rotational temperatures in combination with the expected small change in rotational constants would not give enough experimental data to determine all these constants. An alternative approach is the use of two counterpropagating narrow bandwidth laser beams in a cell. This method has been first demonstrated to work for polyatomic molecules by Riedle et al. [12]. They measured the rotationally resolved, Doppler-free, electronic spectrum of benzene. Since the measurements were performed at room temperature, long rotational progressions could be followed, leading to a precise determination of the rotational constants. Riedle et al. [12] used two lasers with different frequencies in order to eliminate the Doppler-broadened background which is due to the simultaneous absorption of two photons from one laser beam. However, this method introduced an additional (Doppler) broadening of 45 MHz due to the mismatch of the photon's wavevectors and due to the small angle between both laser beams [12]. A few years later, they improved the sensitivity and spectral resolution of their apparatus by performing the two-photon experiments in an external

cavity and using only one laser [13]. In this apparatus, the Doppler-broadened background was less than 1% of the high intensity Doppler-free lines [14].

In this letter, we report a high resolution study on the 0_0^0 band in the $S_1 \leftarrow S_0$ transition of DABCO at room temperature. Two counterpropagating narrow bandwidth ($\sim$ 1 MHz) laser beams (of the same color) are used to excite DABCO in a two-photon excitation scheme. In this way, the rotational transitions could be resolved in the Q-branch.

2. Experimental

A cell was filled with 0.4 Torr DABCO at room temperature. The cell contains three windows. Two windows are mounted collinearly and are used to guide the laser beams through the cell. A third window is mounted at right angles to transmit the collected fluorescence.

To rotationally resolve the LIF spectra a single frequency ring dye laser (Spectra Physics 380D) operating on Rhodamine 110 is used (bandwidth is less than 1 MHz). In order to eliminate the Doppler broadening, which is about 1.3 GHz at room temperature, DABCO has to absorb a photon from each of the two counterpropagating laser beams. The narrow band laser radiation is focussed with a 25 cm lens into the center of the cell. After leaving the cell, the beam is reflected back with a 25 cm spherical mirror, positioned in such a way that the focus of the reflected beam is totally overlapping with the focus of the incoming beam. The total undispersed fluorescence of the DABCO molecules which are electronically excited in this focal region, is imaged on a photomultiplier. To increase the collection efficiency, a spherical mirror is used to reflect the fluorescence in the opposite direction back to the photomultiplier. Since the wavelength of the excitation laser is around 559 nm, and the fluorescence is around 280 nm, stray light can easily be reduced with a cut-off filter (UG 11). The DABCO spectra are recorded together with the transmission peaks of a pressure and temperature stabilized interferometer with a free spectral range of 300 MHz. The absolute frequency of the transmission peaks of the interferometer, and thereby the absolute frequency of the DABCO lines, is determined by the simultaneous recording of the I_2 absorption spectrum [15] in a cell.

The experimental line profile consists of two contributions: a narrow bandwidth component which is the residual Doppler broadening after the absorption of a photon of each of the two counterpropagating laser beams, and a broadband component which is due to the simultaneous absorption of two photons from one laser beam. This broad component gives a continuous background which depends on the density of the rotational lines. The width of the narrow bandwidth component results from the focussing of the laser beams. This width can be calculated from the convergence of the beams, and is about 18 MHz. Other contributions to the experimental linewidth can be estimated to be much smaller: laser linewidth (<1.5 MHz), finite lifetime of the S_1 state of DABCO and pressure broadening (~0.2 MHz) and a finite interaction time of the molecules with the laser radiation (~0.4 MHz).

The overlapping foci of the counterpropagating laser beams are needed to increase the two-photon absorption probability in order to obtain a spectrum with a reasonable signal to noise ratio. However, the alignment of the overlapping foci is critical. Due to mechanical instabilities, this alignment is distorted after about 1 hour, leading to a dramatic decrease in the fluorescence signal. As a result of low signal levels, we can measure only 10 GHz/hour. Therefore we decided to measure the overall contour of the DABCO spectrum with a narrow bandwidth pulsed laser system. In this way, the foci are not needed (the lens is removed, and the spherical mirror is replaced by a planar one), resulting in a less critical alignment, and therefore an improved long term stability of the signal. Radiation from the cw ring dye laser is amplified in a three-stage pulsed dye amplifier (PDA) system (Lambda Physik, LPD 3000) operating on fluorescein 27. The PDA system is pumped by a frequency doubled Q-switched Nd:YAG laser (Spectra Physics GCR 190, 50 Hz repetition rate). The bandwidth of the produced laser radiation is Fourier transform limited and is around 130 MHz. This results in an experimental linewidth of about 200 MHz in the two-photon spectra.

3. Results and discussion

A spectrum of the Q-branch of DABCO has been measured with the PDA-laser system to determine the
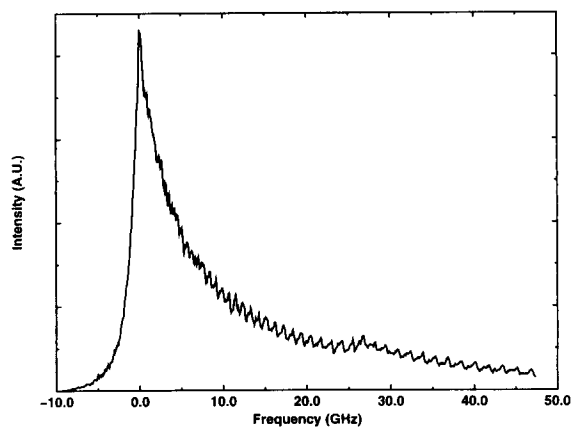

Fig. 1. The Doppler-free two-photon spectrum of the Q-branch of the 0_0^0 band in the $S_1 \leftarrow S_0$ transition of DABCO measured with a resolution of 200 MHz. The absolute frequency of the origin (0 on the scale of the figure) is at $35\,783.23 \pm 0.01$ cm^{-1}.

overall shape of this branch. This spectrum is shown in Fig. 1. The absolute frequency of the sharp feature corresponds to the reported frequency of the origin (ν_0) of this band [4]. The experimental linewidth is estimated to be 200 MHz, and is mainly determined by the laser linewidth. No individual rotational lines are observed. The Q-branch degrades to the blue. In its tail sub-branches become clearly visible when going to higher frequency. A region of about 15 GHz in the less congested part of the Q-branch has been investigated under high resolution. Part of this high resolution spectrum showing one sub-branch ('step') is presented in Fig. 2. Individual rotational transitions are visible. The resolution is about 20 MHz which is mainly attributed to residual Doppler broadening. The intensity pattern is rather irregular. This is not only due to noise, but the main reason is that each sub-branch contains many lines from the adjacent sub-branches.

The origin band of the prolate symmetric top molecule DABCO is a totally symmetric transition having selection rule $\Delta K = 0$. The observed frequencies for the Q-branch ($\Delta J = 0$) are then given by [16]:

$$
\begin{aligned}
\nu = \nu_0 &+ \Delta B J(J+1) + (\Delta A - \Delta B)K^2 \\
&- \Delta D_J J^2(J+1)^2 - \Delta D_{JK}J(J+1)K^2 \\
&- \Delta D_K K^4,
\end{aligned} \tag{1}
$$

with ΔA and ΔB representing the differences between
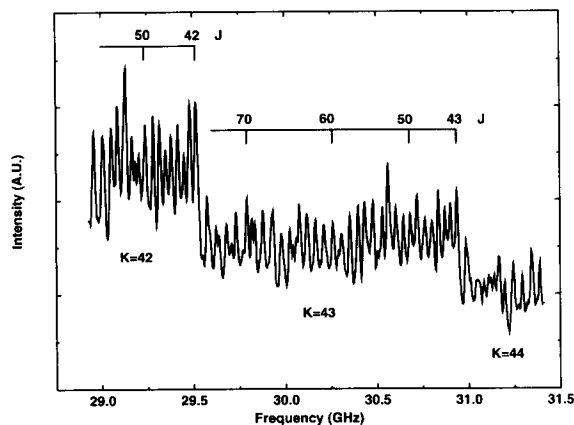
Fig. 2. Part of the high resolution two-photon spectrum of DABCO, showing one 'step' in the Q-branch. The resolution is 20 MHz. The frequency scale is identical to the scale in Fig. 1. Since the selection rules for the origin band are $\Delta J = 0$ and $\Delta K = 0$, individual transitions can be labeled with two quantum numbers J and K.

the rotational constants A and B in the excited state and the ground state ($\Delta A = A' - A''$), all expressed in frequency units, and ν_0 is the frequency between the lowest levels in the S_1 and S_0 states. The last three terms contain the differences in the centrifugal constants D_J, D_{JK} and D_K. J and K are the rotational quantum numbers ($J = 0, 1, 2, ...$ and $K = 0, 1, ..., J$). It is readily seen that fitting the experimental data to Eq. (1) only provides the *change* in rotational and centrifugal distortion constants.

Eq. (1) explains the observed rotational structure. Each sub-branch ('step' in tail of Q-branch) consists of rotational lines with the same K value. The 'edge' of each 'step' can be assigned to the transition $J = K$. Rotational structure within the sub-branch is described by $\Delta B J (J + 1)$. Since the K-sub-branch contains rotational lines with $J > K$ it follows that ΔB is negative. The frequency of the edges of the steps can be approximated (for large J values and small ΔB values) by $\Delta A K^2$. Since the Q-branch degrades to the blue, ΔA is positive.

The complete assignment of the spectrum is now reduced to the assignment of a K value to one of the sub-branches. Simulations of spectra using small values for ΔB and ΔA show that the sharp feature in Fig. 1 represents the origin of the band (within 0.5 GHz). As a next step we made an assignment of the rota-

tional lines, and expressed the J, K quantum numbers of each line with respect to the unknown K value of one of the sub-branches, say K_0. Then we fitted the data to Eq. (1), using the known distance between the origin and the sub-branch which belongs to K_0 (i.e. fixed ν_0) and varying, besides the rotational constants, this unknown K_0 value. The result is the value of K_0 (with an uncertainty of ± 1) and therefore the assignment of the spectra. Table 1 shows the rotational constants obtained from fitting the assigned rotational transitions to Eq. (1). Now the ν_0 value is allowed to vary. The results are shown in Table 1. The precision of the frequencies is limited by thermal drift of the frequency markers during the scan of the laser. The magnitude of this error can be determined by scanning the spectrum several times on various days. A second contribution to the inaccuracy of the rotational constants arises from the uncertainty in the assignment (the K_0 quantum number has an uncertainty of ± 1). This gives an error in the rotational constants which is comparable to that of the error in the frequencies. The errors listed in Table 1 are a combination of both errors. The intensities of the rotational transitions are well described by the J and K independent part of the rotational line strengths [9] and a Boltzmann population distribution at room temperature.

The change in rotational constants are $\Delta A = 16.8$ MHz and $\Delta B = -0.33$ MHz. They have to be compared with the rotational constants in the ground state in order to draw conclusions about the geometrical changes in DABCO. The B'' constant is $B'' = 2509.8 \pm 2.8$ MHz [4]. The A'' constant has not been determined yet. The 0_0^0 band cannot provide information which determines this constant, since this

Table 1
The change in rotational and centrifugal constants of the 0_0^0 band of DABCO ($\Delta A = A' - A''$, etc.). The rotational constant B'' has been determined by Consalvo et al. [4]: $B'' = 2509.8 \pm 2.8$ MHz. The constant A'' has not been determined yet, but can be estimated to be 2630 MHz

molecular constants of the 0_0^0 band of DABCO	
ΔA	16.8(5) MHz
ΔB	−0.33(2) MHz
ΔD_J	−6(3) Hz
ΔD_{JK}	41(12) Hz
ΔD_K	120(60) Hz
band origin	$35\,783.23 \pm 0.01$ cm^{-1}

band has to satisfy the selection rule $\Delta K = 0$. The study of perpendicular ($\Delta K = \pm 1$) vibronic bands in the S_1 state neither provided the A'' constant due to the Coriolis coupling in the degenerate excited state [4]. However, a crude geometry calculation of DABCO shows that A'' is about 2630 MHz. It shows that DABCO is a prolate, near spherical, top. Using these values for the ground state constants, it is seen that upon electronic excitation the A constant increases 0.6% while the B constant remains almost equal. Thus, DABCO is slightly more prolate in the excited state.

In conclusion, it has been shown that Doppler-free two-photon spectroscopy in a cell at room temperature can (partially) resolve the rotational structure of a large polyatomic molecule like DABCO. Analysis of the spectra provide the, in previous studies undetermined, change in rotational constants upon electronic excitation. These changes are found to be quite small, indicating that there is only a slight change in the geometrical structure of DABCO upon electronic excitation.

Acknowledgements

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