High-resolution laser-induced fluorescence study of a cage molecule, 1,4-diazabicyclo[2,2,2]octane, DABCO

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Rotationally resolved laser-induced fluorescence spectra of the caged amine DABCO (1,4-diazabicyclo[2,2,2]octane) seeded in a supersonic He beam are recorded using a high-resolution pulsed dye laser system. Both one-photon and two-photon spectra of the $S_1(A'_1)\rightarrow S_0(A'_1)$ transition are measured. In the one-photon spectra we observe electric quadrupole transitions to the $S_1$ origin and to $a'_1$ vibrational levels and vibrationally induced electric dipole transitions to $a'_2$ and $e'$ vibrational levels. For the first time parallel one-photon transitions with their characteristic rotational structure have been observed. Rotational constants are extracted from both the two-photon and one-photon spectra. The quantum mechanical model previously applied to explain the occurrence of the “memory effect” in fluorescence spectra emanating from the $S_1(e')$ levels is extended here for the $S_1(a'_2)$ levels. Despite the presence of long progressions in several vibrational modes for the $S_1(A'_1)\rightarrow S_0(A'_1)$ transition, the difference in $S_0$ and $S_1$ rotational constants are remarkably small, suggesting that compensating geometry changes take place on excitation to $S_1$.

1. Introduction

In the past much effort has been devoted to investigation of the vibrational structure of the 1,4-diazabicyclo[2,2,2]octane molecule, DABCO, a highly symmetric amine which belongs to the molecular point group $D_{3h}$. No high-resolution excitation spectra have been reported up to now which would clarify ambiguous assignments and/or confirm previous findings based upon low-resolution electronic spectra [1,2]. From the rotational structure observed in the experiment here reported conclusions can be drawn with respect to the symmetry of the vibrational levels involved. Since the DABCO molecule does not possess a permanent dipole moment no information on the geometrical structure can be obtained by microwave spectroscopy. In the present study high-resolution laser-induced fluorescence (LIF) spectroscopy is applied to mode characterization. Additional information concerning the change of geometrical structure upon electronic excitation is obtained.

Transitions from the totally symmetric electronic ground state, $S_0$, to the first electronically excited state, $S_1$, which is also totally symmetric, are one-photon forbidden and two-photon allowed. The forbidden transition becomes partially allowed through an admixture of the nearby $S_2$ state, of $E'$ symmetry, and of another excited state of $A''_2$ symmetry, to the $S_1$ state of $A'_1$ symmetry. Therefore both one- and two-photon spectra are useful to gain insight into symmetry of the active vibrational modes.

The electronic structure and the orbital ordering have been investigated previously [3–5]. The highest filled molecular orbital (HOMO) was found to be the plus combination of lone-pairs, with the minus combination lying almost 2 eV lower in energy. All of the DABCO electronically excited states are Rydberg states in nature, with $(3s)S_1(A'_1)$ at 35783 cm$^{-1}$ and $(3p_{xy})S_2(E')$ at 39814 cm$^{-1}$.

2. Experimental

The experimental setup has been described in detail before [6]. A molecular beam is formed by expanding DABCO (vapor pressure 0.4 Torr at room temperature) seeded in 1.5 atm He or N$_2$ through a pulsed valve with an orifice with a diameter of 1 mm. No significant preferential orientation of the DABCO
molecule in the molecular beam is expected. An unfocused laser beam, 5 mm diameter, crosses the molecular beam perpendicularly 45 mm downstream of the nozzle and induces, via one- or two-photon absorption, the \( S_1 \rightarrow S_0 \) transition in DABCO. For one-photon (two-photon) excitation the polarization of the laser beam is parallel (perpendicular) to the molecular beam axis.

To rotationally resolve the LIF excitation spectrum of DABCO a laser source with high peak power and narrow bandwidth is used. Radiation from a cw ring dye laser (Spectra Physics, 380D) operating on Rhodamine 110 dye is amplified in a home built four-stage pulsed dye amplifier (PDA) system operating on fluorescein 27 dye. The PDA system is pumped by a frequency-doubled Q-switched Nd:YAG laser (Quantel YG681ClO), producing a laser beam with a pulse energy of 100 mJ and a bandwidth of 135 MHz. For one-photon experiments this radiation is frequency doubled in a KDP crystal yielding 20 mJ of UV light. For absolute frequency calibration the \( I_2 \) absorption spectrum is recorded simultaneously with the excitation spectrum. For relative frequency calibration the transmission peaks of a temperature and pressure stabilized interferometer with a free spectra range of 299.41 MHz are recorded.

The laser-induced fluorescence is collected from a 3 mm diameter probe region by a quartz lens system and imaged onto a photomultiplier. In order to reduce the scattered light in the two-photon experiments a Schott UG 11 filter is placed in front of the photomultiplier. The signals are processed by a digital oscilloscope (LeCroy 7400) and a boxcar averager (SRS 250) interfaced with a Personal Computer. The linewidth observed in the experiments is almost completely determined by the residual Doppler broadening of the molecular beam and amounts to 400 and 700 MHz for \( N_2 \) and \( He \) as seeding gas, respectively. The rotational temperature is found to be 1 K for \( He \) and 7 K for \( N_2 \). When argon is used as seeding gas no excitation spectra of DABCO could be observed probably due to massive cluster formation [7].

3. Theoretical aspects

Transitions to the first electronically excited state can be induced by one- and two-photon processes obeying different selection rules [8]. An overview is given in Table 1, where the possible transitions to the \( S_1 \) state are summarized according to the multiplication rules of \( D_{3h} \).

By one-photon excitation only levels of \( e' \) and \( a''_2 \) symmetry can be probed, whereas two-photon transitions involve final states of \( a'_1 \) symmetry. In case of a quadrupole one-photon transition the two-photon selection rules hold.

In a prolate symmetric top molecule like DABCO the transition energy for an excitation from a nondegenerate state to a degenerate state, i.e. for an \( e' \leftrightarrow a'_1 \) transition is given by [9]

\[
\Delta E_{rot} = \nu_0 + B'J'(J' + 1) - B''J''(J'' + 1)
\]
\[+ [A'(1 - 2\zeta) - B'']
\]
\[\pm 2[A'(1 - \zeta) - B']K
\]
\[+ [(A' - B') - (A'' - B'')] K^2. \tag{1}
\]

The upper (lower) sign has to be taken for \( \Delta K = +1 \) \((−1)\) transitions. In the equation above \( J' \) and \( K \) are the rotational quantum numbers and \( A'' \) and \( B'' \) the rotational constants for the ground state \((J' \) for the final state). The transition takes place between levels

<table>
<thead>
<tr>
<th>Selection rules</th>
<th>vibrational</th>
<th>rotational</th>
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<tbody>
<tr>
<td>dipole transition</td>
<td>(</td>
<td>\Delta J</td>
</tr>
<tr>
<td>( a'_1 \rightarrow e' )</td>
<td>(⊥)</td>
<td>(</td>
</tr>
<tr>
<td>( a'_1 \rightarrow a''_2 )</td>
<td>(‖)</td>
<td>(</td>
</tr>
<tr>
<td>quadrupole transition</td>
<td>(</td>
<td>\Delta J</td>
</tr>
<tr>
<td>( J = 1 \leftrightarrow J = 0 )</td>
<td></td>
<td></td>
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2\( h\nu \)

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<tr>
<th>Selection rules</th>
<th>vibrational</th>
<th>rotational</th>
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</thead>
<tbody>
<tr>
<td>( a'_1 \rightarrow a'_1 )</td>
<td>(</td>
<td>\Delta J</td>
</tr>
<tr>
<td>2( \times ) dipole transition</td>
<td>( J = 0 \leftrightarrow J = 0 )</td>
<td>( J = 1 \leftrightarrow J = 0 )</td>
</tr>
</tbody>
</table>
of which one is degenerate; as a consequence the Coriolis coupling $\zeta$ and $l$-doubling terms have to be included in the expression for the level energy. The $l$-doubling is here neglected because in the measured spectra no irregularities for the $K'=1$ levels have been found which normally are taken as evidence of $l$-doubling [9].

For these perpendicular transitions it is readily seen that while the $B$ constant can be determined for the ground and for the excited state, only the difference between the ground state and the excited state value can be quantified for the $A$ constant, see table 2.

For an excitation from a nondegenerate state to a nondegenerate state, i.e. for an $a'_2 \leftrightarrow a'_1$ or for an $a'_1 \leftrightarrow a'_1$ type of transition eq. (1) becomes [9]

$$\Delta E_{\text{rot}} = \nu_0 + B'J'(J' + 1) - B''J''(J'' + 1) + [(A'-B')-(A''-B'')]K^2.$$  (2)

For a parallel dipole transition $|\Delta J|=0$, 1 and for a quadrupole transition $|\Delta J|=0, 1, 2$, the condition $\Delta K=0$ is valid for both. From the selection rules for a quadrupole transition an alternation of intensity (in fact $|\Delta J|=2$ transitions overlap with every second $|\Delta J|=1$) is expected.

From the fit of the experimental data to eq. (1) the following five parameters are obtained: the rotational constants $B''$ and $B'$ for the ground and for the excited state, the rotational constant $A'$ in combination with the Coriolis parameter, $A'(1-\zeta)$, the change of the rotational constant upon excitation, $A'-A''$, and the effective band origin $\nu'_{\chi} + A'(1-2\zeta)B'$, see table 2. The real band origin can be estimated within 6 GHz, see table 3.

For dipole transition the intensities are given by the following expression:

$$I = C_\nu A_{KJ} B_{KJ} \exp\left(-\frac{E_{\text{rot}}}{kT}\right),$$  (3)

where $A_{KJ}$ are the HönL–London factors [9]. The intensities of single rotational lines in the LIF spectrum, assuming a Boltzmann distribution, are essentially determined by the HönL–London factors; the omission of the HönL–London factors did not lead to an acceptable fit.

The intensity of two-photon transitions with $\Delta J=\Delta K=0$ is given by a sum of two terms, as is fully outlined in ref. [8]. For a quadrupole transition one of the two contributions disappears, which explains the lower relative intensity of the Q-branch with respect to the two-photon case. In our spectra we encounter two photon transitions and quadrupole transitions for the same initial and final states, e.g. for the $0_0^+$ band. The quadrupole intensity of the Q branch is much weaker, i.e. the vanishing term gives the dominant contribution.

In these intensity considerations, the influence of spin statistics, $g_{KJ}$ in eq. (3), has been neglected. The twelve equivalent hydrogen spins are assumed to yield a small difference in weight factors, a conjecture sustained by the good intensity fit obtained for our data (better than 10%).

Structural data related to the solid phase of DABCO [4] can be used for comparison. The interatomic distances from ref. [4] are assumed fixed and the appropriate geometry is chosen to be tetrahedral for all the angles. A calculation has been performed to determine the rotational constants in the ground state. The molecule is a prolate, nearly spherical top, if the NCC angle (\(\alpha\)) is tetrahedral. From the calculation performed varying \(\alpha\) follows that a spherical top would require 105° for \(\alpha\) at equilibrium, while the molecule would be an oblate top for \(\alpha < 105°\). The

<table>
<thead>
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<th>Table 2</th>
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<tbody>
<tr>
<td>Molecular constants (in MHz) of some of the observed transitions. The band origins (in cm$^{-1}$) are given with respect to the 0$^0_0^0$ transition at 35783.234 cm$^{-1}$. The error in these values is 0.005 cm$^{-1}$. For the perpendicular transitions, 266 and 276, the effective band origin is given.</td>
</tr>
<tr>
<td>0$^0_0^0$</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>$B''$</td>
</tr>
<tr>
<td>$\Delta B$</td>
</tr>
<tr>
<td>$\Delta A$</td>
</tr>
<tr>
<td>$A'(1-\zeta)$</td>
</tr>
<tr>
<td>$\nu_0$</td>
</tr>
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</table>
Table 3
Observed rovibronic $S_i\rightarrow S_0$ transitions. Rotationally resolved parallel and perpendicular transitions are indicated by $\parallel$ and $\perp$, respectively. Quadrupole transitions are labelled by Q. The band origins are given with respect to the $0_0^0$ transition at 35783.234 cm$^{-1}$. Isotope shifts are indicated by $\Delta^{13}$C and $\Delta^{15}$N. Band origins and isotope shifts are given in cm$^{-1}$. The error in the observed frequencies is 0.005 cm$^{-1}$. Fundamentals are underlined.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>One-photon</th>
<th>Two-photon</th>
<th>Symmetry</th>
<th>Assign.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Q</td>
<td>$\parallel$</td>
<td>$a'_{1u}$</td>
<td>$0_0^0$</td>
<td>$\Delta^{15}$N = -1.571, $\Delta^{13}$C = +2.535 $^a$, fig. 2</td>
</tr>
<tr>
<td>203.762</td>
<td>$?$</td>
<td>$\parallel$</td>
<td>$?+a'_{1u}$</td>
<td>135$^b$</td>
<td>one-photon weak and structureless</td>
</tr>
<tr>
<td>203.56</td>
<td>$?$</td>
<td>$\perp$</td>
<td>$?$</td>
<td>?</td>
<td>weak and structureless</td>
</tr>
<tr>
<td>449.113</td>
<td>$\perp$</td>
<td>$\perp$</td>
<td>$e'$</td>
<td>$27\Sigma^b$</td>
<td>fig. 3a</td>
</tr>
<tr>
<td>670.844</td>
<td>$-$</td>
<td>$\parallel$</td>
<td>$a'_{1u}$</td>
<td>60$^b$</td>
<td>$\Delta^{13}$N = -1.632, $\Delta^{13}$C = -1.489</td>
</tr>
<tr>
<td>671.479</td>
<td>$\parallel$</td>
<td>$\perp$</td>
<td>$a''_{1u}$</td>
<td>$27\Sigma^b + 36\Sigma^b$</td>
<td>weak</td>
</tr>
<tr>
<td>689.506</td>
<td>$\parallel$</td>
<td>$\perp$</td>
<td>$a''_{1u}$</td>
<td>96$^b$ 13$^b$</td>
<td>hot band transition, see table 2 for B$^*$</td>
</tr>
<tr>
<td>691.152</td>
<td>$\perp$</td>
<td>$\perp$</td>
<td>$a''_{1u}$</td>
<td>36$^b$</td>
<td>weak</td>
</tr>
<tr>
<td>777.605</td>
<td>Q</td>
<td>$\parallel$</td>
<td>$a'_{1u}$</td>
<td>50$^b$</td>
<td>fig. 3b</td>
</tr>
<tr>
<td>825.162</td>
<td>$\perp$</td>
<td>$\perp$</td>
<td>$e'$</td>
<td>26$^b$</td>
<td></td>
</tr>
<tr>
<td>882.189</td>
<td>Q</td>
<td>$\parallel$</td>
<td>$a'_{1u}$</td>
<td>40$^b$</td>
<td></td>
</tr>
<tr>
<td>883.080</td>
<td>$\parallel$</td>
<td>$\perp$</td>
<td>$a''_{1u}$</td>
<td>96$^b$ 13$^b$</td>
<td>weak</td>
</tr>
<tr>
<td>897.391</td>
<td>$\perp$</td>
<td>$\parallel$</td>
<td>$e'+a'_{1u}$</td>
<td>$27\Sigma^b$</td>
<td>twophoton weak</td>
</tr>
<tr>
<td>900.51</td>
<td>$\perp$</td>
<td>$\perp$</td>
<td>$e'$</td>
<td>$25\Sigma^b$</td>
<td>weak</td>
</tr>
<tr>
<td>901.070</td>
<td>$-$</td>
<td>$\parallel$</td>
<td>$a'_{1u}$</td>
<td>$35\Sigma^b + 36\Sigma^b$</td>
<td></td>
</tr>
<tr>
<td>919.467</td>
<td>$\parallel$</td>
<td>$\perp$</td>
<td>$a''_{1u}$</td>
<td>17$^b$</td>
<td>$\Delta^{13}$N = -0.945, $\Delta^{13}$C = -1.891, fig. 4</td>
</tr>
<tr>
<td>1011.267</td>
<td>$\perp$</td>
<td>$\perp$</td>
<td>$e'$</td>
<td>24$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Two additional isotopomers are observed shifted by $\Delta (^{13}$C$^{15}$N) = +1.605 cm$^{-1}$ and $\Delta (^{13}$C)$^2 = +1.893$ cm$^{-1}$.

Structure [4] allows to calculate the rotational spectrum once an assumption on the excited state parameters has been made.

Next we discuss the shifts of the band origin arising from isotopic substitution. For the $0_0^0$ band this shift represents the cumulative zero-point effect of isotopic replacement on the 36 vibrational modes. For each mode the amplitude of the motion changes upon isotopic substitution; moreover the motion itself will be modified by symmetry breaking. The two effects are combined and give origin to the observed shifts $\Delta^{13}$C and $\Delta^{15}$N discussed in this context.

For illustration we restrict the discussion to a situation where either the $q_{C-C}$ or $q_{C-N}$ stretch dominates. Upon electronic excitation a softening of the C-C stretch and a stiffening of the C-N stretch has been observed [2,10]. The situation is depicted in figs. 1a and 1b respectively. The vertical dashed lines represent transitions for a molecule where one of the $^{12}$C (or $^{14}$N) is replaced by the heavier isotope. In fig. 1a the result is a blue-shift and in fig. 1b a red-shift.

For a single excited vibration, e.g. $6b_1$, one has to add the effect of the isotopic substitution for this particular mode to obtain the observed isotopic shifts ($\Delta^{13}$C and $\Delta^{15}$N), see table 3.

4. Analysis

In table 3 the measured rovibronic transitions are summarized with their relative experimental uncertainty. Band origins are listed with respect to the $0_0^0$ transition and the type of transition is indicated; Q indicates a quadrupole transition. Bands represented in a separate figure are also indicated.

Final levels of different symmetry can be accessed by using one- and two-photon excitation and since the laser source is of high brightness even quadrupole transitions become observable.

Fig. 2 displays the experimental result for the $0_0^0$ band. The two-photon $0_0^0$ spectrum is displayed in fig. 2a, whereas the $0_0^0$ quadrupole transition is shown in fig. 2b. The most intense features in the two-photon spectrum represent the unresolved Q-branch; the width (fwhm about 1 GHz) is mainly Doppler limited. In section 3 the relative strength of this branch with respect to the $\Delta J \neq 0$ bands is briefly discussed,
First electronically excited state, $S_1$

Ground state, $S_0$

**Fig. 1.** A qualitative potential for a dominant C–C stretching mode is shown in (a). The full lines correspond to DABCO with six $^{12}$C atoms, the dashed ones to the molecule with one $^{13}$C atom substituted by a $^{15}$C (natural abundance 6.6%). The potential well in the $S_0$ state is more shallow, in agreement with the observation of a red-shift upon electronic excitation [1,2]. The isotopic shift is to the blue (vertical dashed line) with respect to the most abundant isotopomer. The situation depicted in (b), corresponding to a potential for a dominant C–N stretch, is reversed with respect to case (a), see refs. [1,2]; therefore a red-shift results from a $^{15}$N substitution (natural abundance 0.8%).

for one-photon quadrupole and two-photon transitions. The low rotational temperature allows observation of rotational levels up to $J = 5$. From the rotational structure the rotational constants $B''$ and $\Delta B$ are derived, see table 2. The width of the $\Delta J \neq 0$ transitions is comparable to that of the Q-branch. The expected intensity alternation between even and uneven $J$ values characterizing the P and R branches is about one to two for low $J$ values, see section 3. In the two-photon spectrum, fig. 2a, the Q-branches of different isotopomers are visible. Replacing one of the C-atoms by $^{13}$C caused an isotope shift $\Delta C = 2.535$ cm$^{-1}$ with an intensity drop to 6.6%. For the $^{15}$N isotopomer a red shift of $\Delta N = -1.571$ cm$^{-1}$ is observed with an intensity drop to 0.8%. Two additional Q-branches of isotopomers are observed shifted by 1.605 cm$^{-1}$ and 1.893 cm$^{-1}$ with intensities of 0.06% and 0.18%, respectively, see table 3. The shift of the isotopomer's Q-branches points to a dominant contribution from the C–C (C–N) stretch for the $^{13}$C($^{15}$N) isotopomer, see section 3.

**Fig. 2.** The LIF spectrum for the $0J_0$ band. In (a) the two-photon $0J_0$ transition is depicted; three Q branches are visible; the two weak ones, blue- and red-shifted, are due to isotopomers. The zero-point energy of all modes is responsible for isotopes shift. Upon substitution $^{12}$C$\rightarrow^{13}$C ($^{14}$N$\rightarrow^{15}$N) the main change occurs in the C–C (C–N) stretching coordinate. The one-photon $0J_0$ transition is reported in (b); the intensity alternation and the absence of the lines adjacent to the band origin are typical of a quadrupole transition, see text.

In table 3 three two-photon transitions to fundamentals of $a'_1$ symmetry are shown, the $\nu'_5$ band at 671 cm$^{-1}$, $\nu'_5$ band at 778 cm$^{-1}$ and the $\nu'_4$ band at 882 cm$^{-1}$. The latter two are also found as one-photon quadrupole transitions. These assignments are new for what concerns $\nu'_2$ and $\nu'_6$ and are based on the assumption that the order of increasing energy does not change upon electronic excitation, taking the $\nu'_4$ band as listed in reference [1,2].

In addition table 3 contains four two-photon tran-
sitions leading to overtone and combination bands of \(a'_1\) symmetry. Naturally, their assignments are rather uncertain, especially because they may be also of mixed character like the \(a'_1\) bands at 897 cm\(^{-1}\) and 901.1 cm\(^{-1}\).

Four one-photon transitions to excited fundamentals of \(e'\) symmetry are listed in table 3, the \(\nu_{27}\) band at 449 cm\(^{-1}\), the \(\nu_{26}\) band at 825 cm\(^{-1}\), the \(\nu_{25}\) band at 900.5 cm\(^{-1}\) and the \(\nu_{24}\) band at 1011 cm\(^{-1}\). Except for the \(\nu_{25}\) band, these assignments are in agreement with previous ones \([1,2]\). If one compares the two perpendicular bands, \(\nu_{27}\) fig. 3a and \(\nu_{26}\) fig. 3b, one notices that the two rotational structures look dissimilar, though belonging to the same band type. In the figure three groups of lines are indicated which have the same rotational assignment. Since one deals with transitions taking place between a nondegenerate ground state, and a degenerate level, the Coriolis coupling has to be taken into account in the expression for the transition energy. Based on the fit of the experimental data it has been concluded that the Coriolis coupling \(\zeta\) undergoes a 30% variation, see table 2, affecting the separation between successive rotational lines belonging to different \(K\) values for the two perpendicular transitions, \(\nu_{26}\) and \(\nu_{27}\).

For an overtone transition \(2'\rightarrow 0''\), with the fundamental of \(e'\) or \(e''\) symmetry, the final level has two possible symmetries (\(a'_1\) and \(e'\)) as shown in table 1. Therefore, both the one- and two-photon spectra contain correlated information for this class of transitions: the level of \(a'_1\) symmetry can be reached by two-photon excitation, the \(e'\) component by one-photon. The relative energies are slightly different, in general. In table 3 we encounter an example for such a behavior. The band at 897 cm\(^{-1}\) (\(2\nu_{27}\)) behaves regularly having a parallel signature for the two-photon spectrum, and a perpendicular signature for the one-photon spectrum. The two origins are relatively shifted by less than 0.005 cm\(^{-1}\).

New are the two assignments of transitions leading to the excitation of vibrations with final \(a''_1\) symmetry, the combination hot band at 690 cm\(^{-1}\) and the \(\nu_{17}\) band at 919 cm\(^{-1}\). These are one-photon parallel transitions, the latter being reassigned. Previously the \(\nu_{23}\) band of \(e'\) symmetry was thought to be responsible for the band at 919 cm\(^{-1}\). However, the high-resolution results of this work not only yield a much more precise value for the band origin, but demand a parallel band assignment. The one-photon transition at 690 cm\(^{-1}\) yields a \(B''\) constant which is off by about 40 MHz from the other \(B''\) values. This is clearly a hot band transition. We suggest that it involves the lowest energy mode, \(\nu_{13}\), and a possible combination band with final symmetry \(a''_1\) is \(9_1^1 13_1^1\), yielding a value for \(\nu'_5\) of \(\approx 750\) cm\(^{-1}\). In addition there are two weak one-photon parallel bands at 671 cm\(^{-1}\) and 883 cm\(^{-1}\); suggested assignments as combination bands are given in table 3.

The two bands at 204 cm\(^{-1}\) and at 206 cm\(^{-1}\) are
Fig. 4. The $\nu_17$ one-photon parallel transition is reported. Note the assigned transitions of the $^{13}$C isotopomer.

difficult to assign. We propose for the two-photon transition at 204 cm$^{-1}$ the torsional overtone $2\nu_{13}$ $(a'_i \rightarrow 0')$. The other bands remain unexplained so far (see table 3).

The isotope shifts observed for $\nu_6$ and $\nu_17$ bands can be considered with respect to the shifts of the $0_0^+$ band, i.e.:

$$\Delta^{15}N(\nu_{17}) - \Delta^{15}N(0_0^+) = 0.626 \text{ cm}^{-1},$$
$$\Delta^{13}C(\nu_{17}) - \Delta^{13}C(0_0^+) = -4.426 \text{ cm}^{-1},$$
$$\Delta^{15}N(\nu_6) - \Delta^{15}N(0_0^+) = -0.061 \text{ cm}^{-1},$$
$$\Delta^{13}C(\nu_6) - \Delta^{13}C(0_0^+) = -4.024 \text{ cm}^{-1}.$$

A cautious conclusion about these differences may be that for both fundamentals the C-N stretch motion is important, with little displacement of the N-atoms.

Table 2 shows that the changes of rotational constants upon electronic excitation are within our experimental accuracy and do not reflect a large variation in geometry upon electronic excitation.

5. Discussion

In the analysis of single vibrational level dispersed fluorescence (SVL) spectra previously reported [11] three categories of decay have been identified for one-photon excitation. Category 1 consists of transitions without memory effect, i.e. final state after fluorescence decay does not contain a vibrational excitation corresponding to the one excited in the $S_1$ state. These are simply $S_1 (e') \rightarrow S_0 (a'_i)$ bands. Category 2, however, leads to a final state where the excited vibration of the $S_1$ state, e.g. of $e'$ symmetry, is found back combined with other vibrations, again of $e'$ symmetry to yield the proper total final symmetry, $a'_i$ symmetry. Category 3 corresponds to a situation very similar to that of category 2; however, extra excitation of $a'_i$ symmetry is also seen in the final state. The low-resolution spectra were recorded for excitation energies containing vibrations assumed to be of $e'$ symmetry [10]. Based on this analysis a correspondence has been determined between ground state and excited state vibrational frequencies [10]. The high-resolution spectra, measured in our laboratory with one and two-photon excitation, shed new light on those results. For three of the four bands we could confirm the previous assignments. In D$_{3h}$ one-photon excitation allows access to levels of $e'$-symmetry (perpendicular transitions) and to levels of $a_1^*$ symmetry (parallel transitions). The fourth band, at 919 cm$^{-1}$, measured with high resolution in the present study, could only be assigned as a state of $a_2^*$ symmetry.

The presence of parallel transitions, i.e. the observation of transitions to states of $a_2^*$ symmetry in the one-photon spectrum of DABCO, including the band at 919 cm$^{-1}$, previously assigned as $\nu_{25}'$, leads to the question of position and identity of the coupling with a state of $A_1^*$ electronic symmetry.

There are two approaches in the literature to the electronically excited states of DABCO. Most often [12-14] the symmetric and anti-symmetric combination of the lone pair orbitals in the ground state $n(+) \text{ and } n(-)$ is simply extended to the excited state Rydberg orbitals, yielding for $n=3$ the 3$s(+)$(A$_1^*$), 3$s(-)(A'_2^*$), 3$p_{xy}(+)$(E$'$), 3$p_{xy}(-)$ (E$''$), 3$p_z(+)$(A''$_1^*$) and 3$p_z(-)$ (A''$_2^*$) excited states. As pointed out by Robin [15], however, this always yields more excited state orbitals than can be accounted for spectroscopically. These observations are based on a wide series of “double” molecules, especially the diones. Robin suggests that Rydberg states even of double (two identical chromophores) molecules should be molecule-centered, yielding for DABCO only the 3$s(A'_1^*)$, 3$p_{xy}(E')$, 3$p_z(A''_2^*)$ $n=3$ states. This single center approach appears to be nicely confirmed in DABCU (diazabicyclo[3,3,3] undecane) [5], the next larger caged amine, where tran-
sitions from \( n(-) \to 3s, 3p_x, \) and \( 3p_z \) are assigned by comparing the one- and two-photon spectra. The \( 3s \) and \( 3p_x \) states of DABCO have been assigned as \( S_1 \) (\( A'_1 \)) at 35783 cm\(^{-1}\) and \( S_2 \) (\( E' \)) at 39814 cm\(^{-1}\), respectively. Thus far there is no direct evidence for the \( 3p_z \) state, which, by analogy with \( \text{NH}_3 \) \[16\] and \( \text{ABCO} \) \[17\], and by ab initio MO theory \[12\], is expected to lie slightly higher than the \( 3p_x \) state. Ito and co-workers \[1\] have observed three optically active Rydberg series in DABCO with quantum defects \( \delta_0 = 0.05, \delta_1 = 0.19 \) and \( \delta_2 = 0.45 \) which can be assigned to \( d, p_x \), and \( p_{xy} \), respectively \[15\]. The \( d \) series is extrapolated to have its lowest \((n=3)\) component, lying 2000 cm\(^{-1}\) higher than the \( 3p_x \) component.

The \( O_{\text{rup}} \) state, which is of \( A' \) symmetry, is expected to lie slightly higher than the \( 3p_x \) state.

To properly describe the decay process the excited state wavefunction has to involve the \( S_1, S_2 \) and \( S_3 \) states, respectively. The initial wavefunction of total \( A''_2 \) symmetry can be written as

\[
\Psi_I = \alpha |S_1(A'_1), n_{p_2} \nu_{p_2}(a''_z)\rangle + \beta |S_2(E'), [n_{p_3} \nu_{p_3}(a''_z) + n_{e_2} \nu_{e_2}(e')] + n_{e_2} \nu_{e_2}(a'_1)\rangle > + \gamma |S_3(A''_2), n_{e_3} \nu_{e_3}(a'_3)\rangle >. \tag{5}
\]

In eq. (5) the combination \( n_{p_3} \nu_{p_3}(a''_z) + n_{e_2} \nu_{e_2}(e') + n_{e_2} \nu_{e_2}(a'_1) \) is of total \( e'' \) symmetry.

The initial vibrational state, \( \nu_{p_2} \), is due to a parallel excitation, \( \nu_{p_3} \) is due to a perpendicular excitation, and \( \nu_{e_2} \) is due to a parallel excitation.

To couple the three electronically excited states of eq. (5) two \( \hat{H}_{\text{mix}} \) operators are needed both of the form \( qQ \),

\[
\hat{H}_{\text{mix}} \propto \langle q(A''_2) Q_{p_2}(a''_z) \rangle \tag{8}
\]

and

\[
\hat{H}_{\text{mix}} \propto \langle q(E') Q_{e_2}(e') \rangle. \tag{9}
\]

Here \( Q \) stands for a normal coordinate of a vibrational mode and \( q \) for an electronic coordinate. These
terms are of the second order in the coordinates, in simplest possible case. If \( n_{r_2} \) is not assumed to be zero in eq. (5) a third-order \( H_{\text{mix}} \) is required.

To discuss DP we first assume \( n_{r_1} = n_{r_3} = n_{r_3} = n_{r_2} = 1 \) and \( n_{r_1} = n_{r_2} = n_{r_3} = 0 \), with \( \rho_1 = \rho_3 \) and \( \rho_1 = \rho_2 \). These decay channels have been observed and are defined as category 2 transitions, see ref. [10].

Alternatively, we are led to category 3 transitions if we put \( n_{r_3} = 0 \) and \( n_{r_1} = n_{r_2} = n_{r_3} = n_{r_2} = n_{r_2} = 1 \).

For category 1 decay there is no “memory effect”; since this channel has also been observed we will discuss it in the following. To this aim eq. (6) is replaced by

\[
\text{DP} \propto | \langle \psi_f | \hat{O}_{\text{dip}} (A^*_2) | \psi_i \rangle |^2.
\]

Explicitly

\[
\text{DP} \propto 2^2 | \langle S_0 (A_1^*) | \hat{O}_{\text{dip}} (A^*_2) | S_3 (A^*_2) \rangle \times \langle n_{r_1} \nu_{r_1} (a_1^*) | n_{r_2} \nu_{r_3} (a_1^*) \rangle |^2.
\]

We have again assumed that the dipole operator \( \hat{O}_{\text{dip}} \) acts only on the electronic coordinates of the molecule. Therefore, in eq. (5) the first and the second term do not contribute to the matrix element of eq. (7). To couple the three electronically excited states of eq. (5) a third-order \( H_{\text{mix}} \) operator is needed

\[
H_{\text{mix,ac}} \propto q (A^*_2) Q_{r_2} (a^*_2) Q_{r_3} (a_1^*).
\]

One has \( \tau_1 = \tau_3 \) with \( n_{r_1} = n_{r_3} = 1 \) and \( n_{r_1} = n_{r_3} = 0 \).

In this way we have demonstrated that the “memory effect” holds also for parallel excitation and yields a similar SVL spectrum as for perpendicular transitions. The band at 919 cm\(^{-1}\) can thus be assigned as \( \nu_{17} \) of \( a^*_2 \) symmetry. Based on this assignment the SVL data yield for the ground state \( \nu_{17} \) the value 986 cm\(^{-1}\). This result is in agreement with the findings of previous investigations [2,10].

6. Conclusions

Analysis of rotational structure in vibronic transitions is well known to yield a wealth of information on molecular properties, particularly on vibrational mode symmetry and molecular geometry. In this paper it is shown that this is also true for a 20 atom molecule such as DABCO, given sufficiently low ro-

References