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TORSIONAL MOTION OF THE CH₃ GROUPS OF PROPANE STUDIED BY RAMAN OVERTONE SPECTROSCOPY

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The Raman spectrum of propane is recorded between 300 and 900 cm⁻¹; first and third overtones are observed with an Ar⁺ laser intracavity setup. This spectrum is analyzed by means of a model with two hindered and coupled methyl rotors. Since the levels probed extend to the region above the torsional barrier (v₃ = 1353 cm⁻¹), all the relevant molecular parameters, in particular the coupling between the methyl rotors, could be accurately determined. By means of a classical approach we have obtained further insight into the qualitative structure of the torsional spectrum.

1. Introduction

For a molecule like H₃C–X–CH₃, the interaction between the two methyl tops seems to be an elusive property. Both tops are equivalent and hindered in their rotation by a three-fold potential barrier. In 1981 Durig [1] has discussed a number of two-top molecules. Whereas the barrier height seemed to be well determined at that time, fine details could not be extracted due to the fact that (a) most spectra were obtained for transitions between relatively low lying states (with respect to the barrier) and (b) strong correlations between certain potential parameters were observed for these low lying states. One of the molecules treated by Durig is propane [2], for which the barrier height is about 1300 cm⁻¹. The mainly used experimental technique was Raman overtone spectroscopy, supplemented by some low resolution IR-absorption measurements. Both methods produce results without rotational structure. For our purposes, i.e. to determine the torsional part of the potential, these coarse techniques are quite useful. Our new asset consists of a significantly increased sensitivity.

For low lying states the torsional motion resembles a vibration around the position of one of the 3×3 potential minima. For highly excited states, i.e. above the potential barrier, the character changes to that of hindered rotations. In fig. 1 an energy level scheme is shown, based upon our experimentally determined parameters, which will be discussed below. This scheme can serve for an introductory discussion as well.

First, we define as a torsional polyad (TP) all levels with the same number of torsional quanta N, distributed as they might be over the two torsional de-
Fig. 1. Energy level scheme, for levels with A symmetry, neglecting tunneling splitting. The dashed line indicates the height of the torsional potential barrier for one top.

Fig. 1. Energy level scheme, for levels with A symmetry, neglecting tunneling splitting. The dashed line indicates the height of the torsional potential barrier for one top.

degrees of freedom, \( N = \nu_1 + \nu_2 \). Polyad \( N \) consists of \( N + 1 \) levels labelled by \( K \). For the highest levels shown these polyads start to mix. For our purposes, however, it turns out to be a very practical classification scheme.

Except for trivial anharmonicity effects, the splittings shown in fig. 1 are mainly due to the interaction between the two tops. We shall call this splitting interaction splitting to distinguish it from tunneling splitting, which cannot be deduced from fig. 1. In view of our limited spectral resolution with a fwhm of about 0.7 cm\(^{-1}\), the latter becomes measurable only for the higher levels.

Our experimental method consists of a redefinition of Durig's measurements; to this end the gas sample is put at the position of a sharp intracavity focus of an Ar\(^+\) laser. Moreover, the sample cell is constructed so that one can work at elevated pressures to gain Raman signal. In addition to eight \( \Delta N = 2 \) Raman transitions, we found with these improvements six \( \Delta N = 4 \) Raman transitions, with most of the final levels above the energy barrier, as indicated in fig. 1. Note that the \( \Delta N = 4 \) transitions are about 50 times weaker than strong \( \Delta N = 2 \) transitions. The work forms a contamination of measurements on \( \text{C}_2\text{H}_6 \) and \( \text{H}_3\text{CCD}_3 \) published previously [3–5].

2. Experimental setup

The experimental setup has already been described before [6,7]. It consists of an Ar\(^+\) laser (Spectra Physics, model 2030-15S) from which the output mirror is removed and replaced by two highly reflecting curved mirrors \((R = 50 \text{ mm}, R = 100 \text{ mm})\), placed adjustably inside the high-pressure sample cell. By changing from an extracavity to an intracavity setup we gained a factor of 80 in Raman intensity. An intracavity power of 300 W could be achieved for the 488 nm laser line. The laser power is stabilized by controlling the light which leaks through the folding mirror \((R = 50 \text{ mm})\) of the cavity. This signal is fed back to the power supply, which controls the current of the discharge.

The high-pressure cell is constructed to stand pressures up to 30 bar. The scattered Raman light, produced in the laser focus (waist of \( 2w_0 = 50 \\mu\text{m} \)), is collected under 90\(^\circ\) with respect to the beam propagation and laser polarization. The focus is imaged by an \(/8\) lens on the entrance slit of a double monochromator (Jobin–Yvon Ramanor HG2S). The four slits of this monochromator are all electronically adjustable. The measurements are performed at a resolution of 0.7 cm\(^{-1}\) (e.g. 50 \( \mu\text{m} \) slitwidth) for the strong transitions \((\Delta N = 2)\) and 2.0 cm\(^{-1}\) (e.g. 200 \( \mu\text{m} \) slitwidth) for the weak transitions \((\Delta N = 4)\). On the opposite side of the focus there is a curved mirror, which reflects the scattered light back to the focus. In this way we gain almost a factor of two in collection efficiency.

The light is measured with a cooled EMI 9862B/350 photomultiplier, which has a S20 spectral response. The output data of the PMT is handled, via a photon counting system (Ortec Brookdeal 5C1), by an Apple Ile computer. This computer also controls the scanning of the gratings of the double monochromator. The frequency is calibrated to several Ar\(^+\) transitions from the discharge inside the laser tube, which are measured during the scan [8]. The accuracy achieved in this way is 0.3 cm\(^{-1}\) for the \( \Delta N = 4 \)
transitions and 0.1 cm\(^{-1}\) for the strongest \(\Delta N=2\) transitions.

The experiments are performed in bulk at a pressure of 3 bar. For higher pressure, light scattering caused severe fluctuations of the power level of the Ar\(^+\) laser. The propane was purchased from J.T. Baker with a 99.5% purity. The Raman spectra are recorded with a scan velocity of 40 cm\(^{-1}\)/h for the \(\Delta N=2\) transitions and 8 cm\(^{-1}\)/h for the \(\Delta N=4\) transitions.

3. Theoretical aspects

The molecular symmetry group of propane is \(G_{36} \cong (C_3 \otimes C_3) \wedge (C_2 \otimes C_4)\) \([1,9,10]\), where \(\otimes\) denotes the direct and \(\wedge\) the semi-direct product of the subgroups. The character table of \(G_{36}\) is given by Bunker \([9]\). The Hamiltonian for the non-rotating \((J=0)\) propane molecule can be written as

$$\hat{H} = F (\hat{P}_{\alpha_1}^2 + \hat{P}_{\alpha_2}^2) + F' \hat{P}_{\alpha_1} \hat{P}_{\alpha_2} + V(\alpha_1, \alpha_2),$$

$$\alpha_1, \alpha_2 \in [-\pi, \pi), \quad (1)$$

with the following Fourier expansion, up to sixth order, for the potential

$$V(\alpha_1, \alpha_2) = \sum_{k=1,2} \left[ \frac{1}{2} V_3 (1 - \cos 3\alpha_k) + \frac{1}{2} V_6 (1 - \cos 6\alpha_k) \right]$$

$$+ \frac{1}{2} V_+ [1 - \cos (3\alpha_1 + 3\alpha_2)]$$

$$+ \frac{1}{2} V_- [1 - \cos (3\alpha_1 - 3\alpha_2)]. \quad (2)$$

The angles \(\alpha_1\) and \(\alpha_2\) describe the torsions about the C–C bonds (see fig. 2). These angles are taken to be zero if a predetermined hydrogen atom of the top lies in the C–C–C plane. The momenta conjugate to the torsional angles are \(\hat{P}_{\alpha_1} = -i\partial/\partial\alpha_1\) and \(\hat{P}_{\alpha_2} = -i\partial/\partial\alpha_2\). The parameters \(V_3\) and \(V_6\) describe the top-frame interaction, whereas \(V_+\) and \(V_-\) describe the anti-gear and geared top-top interactions. The coefficients \(F\) and \(F'\) are determined by the geometrical properties of the molecule only \([11]\). However, because we do not want to rely on a fixed geometry, these coefficients are taken to be parameters, which are optimized as described below, just as the potential parameters \(V_3, V_6, V_+\) and \(V_-\).

It can be readily seen that the Hamiltonian given by eq. (1) is indeed invariant under all operations of \(G_{36}\).

Our notation is somewhat different from that used by Durig et al. \([2]\). The correspondence can be expressed by \(F = \frac{1}{2} \hbar^2 g^{44} = \frac{1}{2} \hbar^2 g^{55}, F' = \hbar^2 g^{45}, V_3 = V_{03}, V_6 = V_{06}, V_+ = \frac{1}{2} (V_{33} - V_{31})\) and \(V_- = -\frac{1}{2} (V_{33} + V_{31})\).

The Hamiltonian \(\hat{H}\) can be separated into three parts:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}, \quad (3)$$

where

$$\hat{H}_k = F \hat{P}_{\alpha_k}^2 + \frac{1}{2} V_3 (1 - \cos 3 \alpha_k)$$

$$+ \frac{1}{2} V_6 (1 - \cos 6 \alpha_k) \quad (k = 1, 2), \quad (4)$$

and

Fig. 2. Equilibrium geometry and torsional angles \(\alpha_1\) and \(\alpha_2\) for propane. Note that positive \(\alpha_k\) are defined clockwise as seen from the central C atom.
Table 1

<table>
<thead>
<tr>
<th>Irrep of G_{36}</th>
<th>Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>\phi_{3v_0}^{1/2}</td>
</tr>
<tr>
<td></td>
<td>\frac{1}{2} \sqrt{(\phi_{3v_0}^{15} + \phi_{3v_0}^{15})}</td>
</tr>
<tr>
<td>A_2</td>
<td>\frac{1}{2} \sqrt{(\phi_{3v_0}^{15} - \phi_{3v_0}^{15})}</td>
</tr>
<tr>
<td>A_3</td>
<td>\frac{1}{2} \sqrt{(\phi_{3v_0}^{15} + \phi_{3v_0}^{15})}</td>
</tr>
<tr>
<td>A_4</td>
<td>\frac{1}{2} \sqrt{(\phi_{3v_0}^{15} - \phi_{3v_0}^{15})}</td>
</tr>
<tr>
<td>E_1</td>
<td>\phi_{v_{3v_1}}^{1/2}, \phi_{v_{3v_1}}^{1/2}</td>
</tr>
<tr>
<td></td>
<td>\frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} + \phi_{v_{3v_1}}^{15})}, \frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} + \phi_{v_{3v_1}}^{15})}</td>
</tr>
<tr>
<td>E_2</td>
<td>\frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} - \phi_{v_{3v_1}}^{15})}, \frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} - \phi_{v_{3v_1}}^{15})}</td>
</tr>
<tr>
<td>E_3</td>
<td>\phi_{v_{3v_1}}^{1/2}, \phi_{v_{3v_1}}^{1/2}</td>
</tr>
<tr>
<td></td>
<td>\frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} + \phi_{v_{3v_1}}^{15})}, \frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} + \phi_{v_{3v_1}}^{15})}</td>
</tr>
<tr>
<td>E_4</td>
<td>\frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} - \phi_{v_{3v_1}}^{15})}, \frac{1}{2} \sqrt{(\phi_{v_{3v_1}}^{15} - \phi_{v_{3v_1}}^{15})}</td>
</tr>
<tr>
<td>G</td>
<td>\phi_{v_{3v_1}}^{1/2}, \phi_{v_{3v_1}}^{1/2}, \phi_{v_{3v_1}}^{1/2}</td>
</tr>
</tbody>
</table>

\hat{H}_{12} = \hat{F} \cdot \hat{P}_{\alpha_1} \cdot \hat{P}_{\alpha_2} + \frac{1}{2} V_+ \left[ 1 - \cos(3\alpha_1 + 3\alpha_2) \right]
+ \frac{1}{2} V_- \left[ 1 - \cos(3\alpha_1 - 3\alpha_2) \right].  \tag{5}

In order to diagonalize \( \hat{H} \), we first diagonalize \( \hat{H}_k \) (single-top problem) in the orthonormal basis
\[
\psi_{3n_k + \sigma_k}(\alpha_k) = \frac{1}{\sqrt{2\pi}} \exp\left\{ i (3n_k + \sigma_k) \alpha_k \right\},  \tag{6}
\]
with \( \sigma_k = 0, \pm 1 \) and \( n_k = 0, \pm 1, \ldots, \pm n_{\text{max}} \). The use of \( \sigma_k \) is convenient because the basis functions for a given \( \sigma_k \) span the irreducible representations (irreps) \( \Gamma^1 \) \((\sigma_k = 0)\), \( \Gamma^2 \) \((\sigma_k = -1)\) and \( \Gamma^3 = \Gamma^{3*} \) \((\sigma_k = 1)\) of the subgroup \( C_3 \) of \( G_{36} \). In this way we achieve a block factorization of the Hamiltonian matrix into three blocks. Note that the above diagonalization needs to be carried out only once, because \( \hat{H}_1 \) and \( \hat{H}_2 \) have identical forms. Taking into account only the lowest \( v_{\text{max}} \) eigenvectors \( A \) of the single-top problem, which are real, we can create an orthonormal basis \( \psi_{3n}^{v_{1/2}} \) for the total two-top Hamiltonian \( \hat{H} \).
\[
\phi_{\alpha_1 \alpha_2}^{v_{1/2}}(\alpha_1, \alpha_2) = \sum_{\sigma_1, \sigma_2} A_{3n_1 + \sigma_1}^{v_1} A_{3n_2 + \sigma_2}^{v_2} \psi_{3n_1 + \sigma_1}(\alpha_1) \psi_{3n_2 + \sigma_2}(\alpha_2),  \tag{7}
\]
with \( \sigma_k = 0, \pm 1 \) and \( v_k = 0, \ldots, v_{\text{max}} - 1 \) \((k = 1, 2)\), where \( v_k \) denotes the number of torsional quanta present in the \( k \)th rotor. From these basis functions we can project bases of the irreps of \( G_{36} \) (see table 1), giving 16 blocks in the Hamiltonian matrix. Diagonalizing these blocks yields the eigenstates of the system. The eigenstates can now conveniently be labelled by \( |\nu \Gamma \rangle \), where \( \Gamma \) is an irrep of \( G_{36} \) and \( \nu \) a quantum number labelling the different states belonging to \( \Gamma \).

In order to obtain the relative Raman intensities \[12\], we calculate the transition matrix elements \( \langle \nu' \Gamma | \alpha | \nu \Gamma \rangle \) between the eigenstates \( |\nu \Gamma \rangle \) obtained previously. For the isotropic polarizability \( \alpha \) we assume the following dependence on the torsional angles (the first non-vanishing terms in the Fourier expansion)
\[
\alpha \propto \cos 3\alpha_1 + \cos 3\alpha_2.  \tag{8}
\]

The results are compared directly to the measured relative intensities, thus neglecting the effect of the anisotropy in the polarizability. The eigenstates \( |\nu \Gamma \rangle \) are occupied according to a Boltzmann distribution at \( T = 300 \) K. Because the isotropic polarizability is an irreducible tensor operator of rank zero (scalar) it belongs to the irrep \( A_1 \) of \( G_{36} \). As a consequence it can only induce Raman transitions between levels belonging to the same irrep of \( G_{36} \). To obtain the pa-
rameters in the Hamiltonian (eq. (1)) from the experimental spectrum we minimized the squared difference between the calculated frequencies $\nu_{i}^{\text{calc}}$ and the experimental frequencies $\nu_{i}^{\text{exp}}$, where $i$ corresponds to the transition $|\nu\Gamma\rangle \rightarrow |\nu'\Gamma\rangle$, considering the expression

$$
\left[ \sum \left( \nu_{i}^{\text{calc}} - \nu_{i}^{\text{exp}} \right) w_{i} \right]^{1/2}.
$$

(9)

The weight factors $w_{i}$ are taken to be the inverse of the experimental uncertainties.

The error in the parameters is determined in the following way. Starting from the frequencies $\nu_{i}^{\text{exp}}$, we shift these frequencies by a random amount $\Delta$ within the experimental error range of that specific frequency. With the new frequencies $\nu_{i}^{\text{exp}} + \Delta$, a new set of parameters has been obtained using the above-mentioned minimization procedure. If this process is repeated a number of times the error in a certain parameter will equal the standard deviation of the values generated for that parameter.

If we consider propane as a nearly-rigid molecule (as in section 5), its molecular symmetry group would be $G_{4} \cong C_{3v} \otimes C_{2} \cong C_{6v}$. The torsional motions become normal vibrations of type $A_{2}$ and $B_{1}$ within this group. The levels $N_{K}$ (see fig. 1), given by these normal vibrations, can be labelled within the group $G_{4}$ as

$$
\Gamma_{N_{K}} = (A_{2})^{N-K+1} \otimes (B_{1})^{K-1}
$$

$$
= A_{1}, \quad N \text{ even, } K \text{ odd},
$$

$$
= A_{2}, \quad N \text{ odd, } K \text{ odd},
$$

$$
= B_{1}, \quad N \text{ odd, } K \text{ even},
$$

$$
= B_{2}, \quad N \text{ even, } K \text{ even}.
$$

(10)

The reverse correlation [9] between $G_{4}$ and $G_{36}$ (table 2) makes it easy to indicate the correlation between the levels $N_{K}$ and the eigenkets $|\nu\Gamma\rangle$.

4. Results and discussion

In fig. 3 we show the two parts of the spectrum where the torsional transitions are measured. On the left side of fig. 3a the $\nu_{9}$ C–C–C bending mode at 369.6 cm$^{-1}$, which is very intense compared to the torsional overtone transitions, causes a steep rise. In the frequency range 530–675 cm$^{-1}$ no torsional overtone transitions were observed. The torsional transitions in fig. 3b are measured on the flank of the

<table>
<thead>
<tr>
<th>$G_{4}$</th>
<th>$G_{36}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1}$</td>
<td>$A_{1} \otimes E_{1} \otimes E_{2} \otimes G$</td>
</tr>
<tr>
<td>$A_{2}$</td>
<td>$A_{2} \otimes E_{1} \otimes E_{2} \otimes G$</td>
</tr>
<tr>
<td>$B_{1}$</td>
<td>$A_{1} \otimes E_{1} \otimes E_{2} \otimes G$</td>
</tr>
<tr>
<td>$B_{2}$</td>
<td>$A_{2} \otimes E_{1} \otimes E_{2} \otimes G$</td>
</tr>
</tbody>
</table>

Table 2

Reverse correlation between $G_{4}$ and $G_{36}$

![Fig. 3. Raman spectra of propane for the (a) $\Delta N=2$ and (b) $\Delta N=4$ transitions. The solid lines represent the experimental spectra and the dashed lines the theoretical spectra with a fwhm of 3.2 cm$^{-1}$. In (a) the highest (lowest) experimental intensity corresponds with 12000 (400) counts. In (b) the corresponding numbers are 3200 and 2300.](image-url)
The transitions marked with an asterisk have not been used to fit the parameters of the torsional Hamiltonian (eq. (1)). The reason is that the observed peaks are composed of two or more transitions with different intensity; the intensities can only be estimated using eq. (8). In the calculated spectra of figs. 3a and 3b the corresponding peaks are the sum of the estimated intensities. All parameters found from this fit and used to calculate the torsional Raman spectrum are listed in table 5. The values for the kinetic coefficients \( F \) and \( F' \) are in reasonable agreement with the values of Durig et al. [2], calculated from an assumed structure. Note that our \( F' \) corresponds to \( h^2g^{45} \) of ref. [2].

Table 3

<table>
<thead>
<tr>
<th>Observed Raman shift (cm(^{-1}))</th>
<th>Observed intensity (^{a)})</th>
<th>Assignment (^{b)})</th>
<th>Calculated Raman shift (cm(^{-1}))</th>
<th>Calculated intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>369.6(1)</td>
<td>-</td>
<td>( \nu_6 ) bend</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>383.5(3)</td>
<td>0.54</td>
<td>1_2 \rightarrow 3_2</td>
<td>383.23</td>
<td>0.46</td>
</tr>
<tr>
<td>393.4(2)</td>
<td>0.48</td>
<td>1_1 \rightarrow 3_1</td>
<td>412.39</td>
<td>1.38</td>
</tr>
<tr>
<td>423.0(1)</td>
<td>0.25</td>
<td>0_1 \rightarrow 2_1</td>
<td>423.05</td>
<td>1.43</td>
</tr>
<tr>
<td>467.2(2)</td>
<td>0.65</td>
<td>2_2 \rightarrow 4_2</td>
<td>468.61</td>
<td>0.35</td>
</tr>
<tr>
<td>486.5(2)</td>
<td>1.02</td>
<td>1_1 \rightarrow 3_1</td>
<td>487.56</td>
<td>0.57</td>
</tr>
<tr>
<td>506.2(1)</td>
<td>0.89</td>
<td>1_2 \rightarrow 3_2</td>
<td>505.62</td>
<td>0.82</td>
</tr>
<tr>
<td>521.2(1)</td>
<td>1.00</td>
<td>0_2 \rightarrow 2_2</td>
<td>521.61</td>
<td>1.00</td>
</tr>
<tr>
<td>686.9(3)</td>
<td>0.64 \times 10^{-1}</td>
<td>2_2 \rightarrow 6_2(\text{E}_1, \text{E}_4, \text{G})</td>
<td>688.19</td>
<td>0.45 \times 10^{-1}</td>
</tr>
<tr>
<td>693.7(3)</td>
<td></td>
<td>3_1 \rightarrow 7_1(\text{A}_2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>702.8(3)</td>
<td>0.15 \times 10^{-1}</td>
<td>2_1 \rightarrow 6_1(\text{E}_2)</td>
<td>703.32</td>
<td>0.83 \times 10^{-1}</td>
</tr>
<tr>
<td>708.5(3)</td>
<td>0.16 \times 10^{-1}</td>
<td>1_2 \rightarrow 5_2(\text{E}_1, \text{E}_4)</td>
<td>708.21</td>
<td>0.97 \times 10^{-1}</td>
</tr>
<tr>
<td>718.8(3)</td>
<td>0.21 \times 10^{-1}</td>
<td>3_2 \rightarrow 7_2(\text{A}_2) (^{f)})</td>
<td>716.56</td>
<td>0.35 \times 10^{-1}</td>
</tr>
<tr>
<td>728.4(3)</td>
<td>0.62 \times 10^{-2}</td>
<td>2_1 \rightarrow 5_2(\text{A}_2, \text{G})</td>
<td>728.82</td>
<td>0.34 \times 10^{-1}</td>
</tr>
<tr>
<td>736.0(5)</td>
<td></td>
<td>1_1 \rightarrow 5_1(\text{E}_2, \text{E}_3, \text{G})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>748.6(3)</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>758.6(3)</td>
<td>0.38 \times 10^{-1}</td>
<td>1_1 \rightarrow 5_1(\text{E}_2, \text{E}_3, \text{G})</td>
<td>758.92</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\(^a\) Relative to the 0_1 \rightarrow 2_1.

\(^b\) The notation is explained in section 4; if \( \Gamma \) is not specified, the four \( \Gamma \) blocks lead to undistinguishable transitions.

\(^c\) Shoulder (see fig. 3a). \(^d\) Not used in the fit. \(^e\) Possible \( \nu_6 \) combination band (see section 4).

\(^f\) The 7_1 level contains a strong admixture from the 6th polyad; therefore, this transition, which does not seem to be a \( \Delta N = 4 \) one, is allowed. For the same reason, the assignment of \( N \) becomes somewhat arbitrary for the 7_3 and 7_4 levels.
Table 4

| $|\nu T\rangle$ representation for the torsional levels, with their calculated energies, $n_{\text{max}} = 15$, $\nu_{\text{max}} = 10$. The levels are ordered according to the symmetry classification of section 3 |
|---|---|---|---|---|---|---|
| $N_\kappa$ | $|0A_1\rangle$ | $|0E_1\rangle$ | $|0E_2\rangle$ | $|1G\rangle$ | $|1A_2\rangle$ | $|1E_4\rangle$ | $|1E_5\rangle$ | $|1E_6\rangle$ | $|1E_7\rangle$ | $|1G_4\rangle$ |
| $0_1$ | 246.37 | 246.37 | 246.37 | 246.37 | 246.37 | 246.37 | 246.37 | 246.37 | 246.37 | 246.37 |
| $1_1$ | 460.05 | 460.05 | 460.05 | 460.05 | 460.05 | 460.05 | 460.05 | 460.05 | 460.05 | 460.05 |
| $1_2$ | 510.94 | 510.94 | 510.94 | 510.94 | 510.94 | 510.94 | 510.94 | 510.94 | 510.94 | 510.94 |
| $2_1$ | 669.43 | 669.43 | 669.43 | 669.43 | 669.43 | 669.43 | 669.43 | 669.43 | 669.43 | 669.43 |
| $2_2$ | 705.97 | 705.97 | 705.97 | 705.97 | 705.97 | 705.97 | 705.97 | 705.97 | 705.97 | 705.97 |
| $3_1$ | 737.63 | 737.63 | 737.63 | 737.63 | 737.63 | 737.63 | 737.63 | 737.63 | 737.63 | 737.63 |
| $3_2$ | 812.47 | 812.47 | 812.47 | 812.47 | 812.47 | 812.47 | 812.47 | 812.47 | 812.47 | 812.47 |
| $3_3$ | 894.35 | 894.35 | 894.35 | 894.35 | 894.35 | 894.35 | 894.35 | 894.35 | 894.35 | 894.35 |
| $3_4$ | 1016.53 | 1016.53 | 1016.53 | 1016.53 | 1016.53 | 1016.53 | 1016.53 | 1016.53 | 1016.53 | 1016.53 |
| $4_1$ | 1061.66 | 1061.66 | 1061.66 | 1061.66 | 1061.66 | 1061.66 | 1061.66 | 1061.66 | 1061.66 | 1061.66 |
| $4_2$ | 1071.91 | 1071.91 | 1071.91 | 1071.91 | 1071.91 | 1071.91 | 1071.91 | 1071.91 | 1071.91 | 1071.91 |
| $4_4$ | 1175.52 | 1175.52 | 1175.52 | 1175.52 | 1175.52 | 1175.52 | 1175.52 | 1175.52 | 1175.52 | 1175.52 |
| $4_5$ | 1255.37 | 1255.37 | 1255.37 | 1255.37 | 1255.37 | 1255.37 | 1255.37 | 1255.37 | 1255.37 | 1255.37 |
| $5_1$ | 1219.00 | 1219.00 | 1219.00 | 1219.00 | 1219.00 | 1219.00 | 1219.00 | 1219.00 | 1219.00 | 1219.00 |

$^a$) Four more levels are calculated for every $\Gamma$ block, but because of the polyad mixing it is no longer possible to indicate their $N_\kappa$ character (first column). The last two rows contain the levels indicated as $7_3$ and $7_4$ in table 3.

The potential is symmetric with respect to the reflections $\alpha_1 \equiv \alpha_2$ and $\alpha_1 \equiv -\alpha_2$, because the corresponding operations belong to $G_{36}$. From fig. 4 it seems that the potential is also symmetric with respect to the reflection $\alpha_1 \equiv -\alpha_1$ or $\alpha_2 \equiv -\alpha_2$. This is only approximately so, because the corresponding operations do not belong to $G_{36}$.

In fig. 5 four probability densities of eigenfunctions of the torsional hamiltonian (eq. 11) are drawn, superimposed on the potential surface of fig. 4. The eigenfunctions belonging to figs. 5a, 5b and 5c, 5d have energies close to and well below $V_3$, respectively. In figs. 5c and 5d the molecule wiggles around the potential minimum. When the energy is
Table 5
Torsional potential constants and kinetic coefficients (cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>Value a)</th>
<th>Error</th>
<th>Value b)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_3$</td>
<td>1353</td>
<td>2</td>
<td>1323.4</td>
<td>9.6</td>
</tr>
<tr>
<td>$V_6$</td>
<td>18.9</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_+^e$</td>
<td>-143</td>
<td>2</td>
<td>-154.3</td>
<td>7.8</td>
</tr>
<tr>
<td>$V_-^e$</td>
<td>-40.4</td>
<td>0.8</td>
<td>-22.3</td>
<td>7.8</td>
</tr>
<tr>
<td>$F$</td>
<td>5.72</td>
<td>0.01</td>
<td>6.1021</td>
<td>d)</td>
</tr>
<tr>
<td>$F'$</td>
<td>-1.58</td>
<td>0.02</td>
<td>-1.4335</td>
<td>d)</td>
</tr>
</tbody>
</table>

a) Our result (see section 4). b) Durig et al. [2].
c) See section 3.
d) Calculated from an assumed structure by Durig et al. [2].

Fig. 4. Torsional potential for propane. The numbers indicating the contour lines are energy values in wavenumbers.

close to the torsional barrier, the molecule can tunnel through the barrier and move from one well to another.

The eigenfunctions are symmetric or antisymmetric with respect to exchange of excitation between rotors 1 and 2 (besides those belonging to $\Gamma = G$, see table 1). For instance, to the levels $1_1$ and $1_2$ of $\sigma_1 = \sigma_2 = 0$ ($\Gamma = A_3$ and $A_2$, respectively) belong with high accuracy to the eigenfunctions $\frac{1}{\sqrt{2}}[|10\rangle \pm |01\rangle]$. Here, $|1_1 1_2 \rangle = |10\rangle$ indicates one torsion quantum in rotor 1 and zero in rotor 2 (see figs. 5c and 5d). For higher levels the situation becomes more complex, since many more states of the type $|v_1 v_2\rangle$ contribute to the eigenfunctions. However, for increasing excitation, the lowest level of a polyad regain part of their simplicity, due to the anharmonicity of the single rotor barrier potential. For instance, the $|50\rangle$ excitation is degenerate with the $|05\rangle$ excitation, but not with the $|41\rangle$ or $|32\rangle$ ones. This regained simplicity is shown in figs. 5a and 5b. The $S_1^e (A_3)$-level possesses an eigenfunction whose probability density shows six maxima along the $\alpha_1$ axis; i.e. the five nodes of a $|50\rangle$ excitation are present. Fig. 5a is symmetric with respect to exchange $\alpha_1 = \alpha_2$; therefore, the same five nodes are visible along the $\alpha_2$ axis. The $V_+$ and $V_-^e$ terms slightly distort the picture in the sense that both $\alpha_1$ and $\alpha_2$ being positive or negative correspond to a preferred situation. Fig. 5b corresponds to the antisymmetric case. Therefore, along the diagonal $\alpha_1 = \alpha_2$ one finds a vanishing probability. Except for this main change, the figures look very similar.

From fig. 1 it can be seen that the average energies of the torsional levels of the different polyads start to come closer together as the energy of the polyads approaches the barrier top. This is in accordance with what is found for $\text{H}_2\text{CCH}_3$ and $\text{H}_2\text{CCD}_3$ [3,4]. We expect the levels far above the barrier to behave like rotational levels.

It is also evident from fig. 1 that the lowest levels of each polyad tend to group into pairs of nearly degenerate levels, for higher excitation. The remaining splitting $\Delta E$ determines the time, $\tau = \hbar / \Delta E$, a molecule needs to get the torsional excitation transferred from one end of the molecule to the other, if one starts from a situation in which one of the two rotors is excited. The higher the excitation the longer this transfer time. For instance, $\tau$ changes from 0.1 ps for $N = 1$ to 1 ps for $N = 6$. This transfer rate depends on the molecule in question. For propane, the intermediate $\text{CH}_2$ group and the molecular dimensions determine the rate of the top-top energy transfer.

Analysis of the eigenvectors of the total Hamiltonian (eq. (11)) shows that the peaks at 708.5 and 728.4 cm$^{-1}$ correspond to transitions to the levels $S_2$; these $S_2$ levels are split by 19.9 cm$^{-1}$ due to tunneling (table 3). Thus, tunneling effects become visible if the levels approach or exceed the torsional barrier. In our fitting program tunneling is taken into account. For low lying levels tunneling splitting becomes negligible compared to our resolution of about 1 cm$^{-1}$.
In the measured spectrum there are some unassigned features. In the following we are going to speculate about their possible origins. The fact that we cannot present a definite argument, in the end, does not affect the fit discussed as the main result of this paper. In addition one has to keep in mind that we deal with very weak Raman transitions altogether. Therefore, small concentrations of impurities with strong Raman transitions readily produce spurious transitions.

In our analysis we have not taken into account a coupling between the C–C–C bending mode ($A_1$ symmetry) and the torsional motion. This coupling arises from mutual hindrance of the CH$_3$ rotations which diminishes if the C–C–C bending angle opens up for certain positions of the CH$_3$ tops. This coupling affects only members of the polyads which (a) possess $A_1$ symmetry and (b) are energetically nearly degenerate with the $\nu_9$ levels. The main candidate to be influenced by this coupling seems to be the $2\Gamma_1 (A_1)$ level about 50 cm$^{-1}$ above the first excited $\nu_9$ level.

If we search for effects of this kind in figs. 3a and
Raman overtone spectroscopy of propane

In 3b, we see that the calculated transition $2_1 \rightarrow 6_1$ at 703.3 cm$^{-1}$ might show a red-shifted component, which could explain the observed peak at 693.7 cm$^{-1}$. However, this transition is not of $A_1$ symmetry and therefore we can disregard this idea to explain either of the two unassigned lines at 693.7 and 748.6 cm$^{-1}$.

Coupling between the bending mode and torsional motion may result also in the observation of combination bands like $0_1 \rightarrow \nu_9 + 2_1$. This hypothesis does not work either; torsional Raman transitions (between levels of $A_1$ symmetry) should reappear shifted to the blue by about 369 cm$^{-1}$. Actually, a number of transitions has been observed shifted by nearly 369 cm$^{-1}$. Since the observed transitions are not all between levels of $A_1$ symmetry, we disregard this hypothesis as well.

However, not only Fermi-resonance-like coupling may lead to observable combination bands. Remember that intensities for Raman transitions were derived from a very simple ansatz, $a = \text{const.} (\cos 3\alpha_1 + \cos 3\alpha_2)$, eq. (8). The constant factor in front of the bracket may be thought of as a first term of a series expansion. A (smaller) term proportional to $q_9 (\cos 3\alpha_1 + \cos 3\alpha_2)$ will appear in that same series, which will produce combination tone transitions for each symmetry of the torsional levels concerned. Here, $q_9$ stands for the normal coordinate of the C–C–C bending motion ($A_2$ symmetry). These combination bands either yield Raman signals at the position of hitherto unassigned Raman peaks or find an "excuse" like being under a strong plasma line or drowned in a strong background. In two cases shoulders of nearby Raman transitions may indicate their presence. The transition at 736 cm$^{-1}$ has been measured with the Ar$^+$ 514 nm transition in order to avoid coincidence with the plasma line. In these measurements a weak separate peak has been observed. As to the intensity of these combination bands, note that the observations concern intensities approximately a factor of 100 weaker than strong two-photon transitions. Thus we have presented a possible assignment for the peaks at 693.7 and 748.6 cm$^{-1}$.

As the only clearly determined impurity of our gas sample we identified isobutane. Gas-chromatographic measurements yielded a concentration of about 0.1% of this impurity in propane. The Raman spectrum of isobutane possesses an extremely strong transition ($\nu_8$) at 799 cm$^{-1}$, which has been observed on the red flank of the $\nu_9$ fundamental of propane at 867 cm$^{-1}$. The isobutane signal was found to be 200 times weaker than this $\nu_9$ transition. In addition, a 20 times weaker isobutane signal at 433 cm$^{-1}$ ($\nu_8$ mode). Both these observations agree with an isobutane concentration of 0.1–0.5%.

5. A qualitative approach to the torsional spectra

5.1. General remarks

Recently a qualitative approach to treat the polyadic rotational and vibrational spectra was proposed based on the analysis of the classical Hamiltonian function corresponding to the effective Hamiltonian for a polyad [13]. It permits us to predict and to explain the main features of the polyads such as the existence of regular sequences of levels within the polyads and the quasi-degeneracies of levels forming these sequences. Moreover, it permits us to localize the positions of these regular sequences of levels within polyads.

This approach also predicts that with energy increase the polyads will typically undergo qualitative changes (rearrangements), and relates these changes to certain bifurcations in the corresponding classical problem. A well-known example of such rearrangements is e.g. the transition from the normal to the local modes in the overtone stretching spectra of molecules containing several bonds.

Here we use this qualitative approach to treat the torsional Raman spectra of propane. In this case we deal with two tops and high barriers for internal rotation and it is possible to neglect the effect of the tunneling splitting of the torsional levels below the barrier, which reduces the problem to the usual vibrational one treated in ref. [13].

5.2. Application to propane

First, we neglect tunneling and approximate the potential (eq. (2)) by its Taylor series around the potential minimum at $\alpha_1 = \alpha_2 = 0$, truncated at the fourth-order terms. This leads to a potential for two coupled anharmonic oscillators,
\[ V(\alpha_1, \alpha_2) = a_1(\alpha_1^2 + \alpha_2^2) + a_2\alpha_1\alpha_2 + a_3(\alpha_1^4 + \alpha_2^4) + a_4(\alpha_1^2 + \alpha_2^2)\alpha_1\alpha_2 + a_5\alpha_1^2\alpha_2^2, \]

where the parameters \(a_n\) are related to those in eq. (2) by

\[ a_1 = \frac{2}{3}(V_3 + 4V_6 + V_+ + V_-) = 2801.7 \text{ cm}^{-1}, \]
\[ a_2 = \frac{2}{3}(V_+ - V_-) = -461.7 \text{ cm}^{-1}, \]
\[ a_3 = -\frac{22}{16}(V_3 + 6V_6 + V_+ + V_-) = -2484.0 \text{ cm}^{-1}, \]
\[ a_4 = -\frac{22}{4}(V_+ + V_-) = 692.6 \text{ cm}^{-1}, \]
\[ a_5 = -\frac{22}{4}(V_+ + V_-) = 1238.0 \text{ cm}^{-1}, \]

The numerical values correspond to the case of propane if we utilize the parameters of table 5. To simplify the application of the theory we introduce new variables

\[ Q_k = \left(\frac{a_1}{F}\right)^{1/4} \alpha_k, \quad \tilde{P}_k = \left(\frac{F}{a_1}\right)^{1/4} \tilde{P}_{\alpha_k}, \]

and we rewrite the truncated torsional Hamiltonian in the form

\[ \frac{\tilde{H}}{2\sqrt{F}} = \frac{1}{2}(\tilde{P}_1^2 + \tilde{P}_2^2 + Q_1^2 + Q_2^2) + A\tilde{P}_1\tilde{P}_2 + BQ_1Q_2 + E(Q_1^2 + Q_2^2) + G(Q_1^2 + Q_2^2)Q_1Q_2 + UQ_1^2Q_2^2, \]

well suited for further qualitative analysis. Here, for convenience's sake, we have used the same notation for the coefficients as in ref. [13]. One finds:

\[ A = \frac{1}{2}F = -0.138, \quad B = \frac{1}{2}a_2 \frac{a_1}{a_1} = -0.082, \]
\[ E = \frac{1}{2}a_3 \sqrt{\frac{F}{a_1}} = -0.020, \]
\[ G = \frac{1}{2}a_4 \sqrt{\frac{F}{a_1}} = 0.0056, \]
\[ U = \frac{1}{2}a_5 \sqrt{\frac{F}{a_1}} = 0.010. \]

Neglecting interaction between the torsional polynomials (TPs), we construct an effective Hamiltonian (\(\tilde{H}_{\text{eff}}\)). The way to do this is well established. First, we have to rewrite expression (14) for the total Hamiltonian in terms of operators \(a_1^\dagger, a_k\ (k=1, 2)\) defined by

\[ Q_k = (a_1^\dagger + a_k)/\sqrt{2}, \]
\[ P_k = i(a_1^\dagger - a_k)/\sqrt{2}. \]

The Hamiltonian thus obtained must be transformed using the well-known canonical transformation techniques. Taking into account only the \(N\)-conserving contributions from the different terms in eq. (14) we arrive [13] at the following expression for \(\tilde{H}_{\text{eff}}\):

\[ \frac{\tilde{H}_{\text{eff}}}{2\sqrt{F}a_1} = \tilde{H}_0 + (s_1 + \frac{1}{2} s_2) J_x + s_2 J_x + t J_x^2 + u J_x^2, \]

where

\[ s_1 = A + B = -0.220, \quad s_2 = 3G = 0.017, \]
\[ t = U = 0.010, \quad u = (6E - U)/2 = -0.065. \]

\(J_x, J_z\) and \(\tilde{J}\) are the Schwinger pseudomomentum operators defined by

\[ J_x = (a_1^\dagger a_2 + a_2^\dagger a_1)/2, \]
\[ J_z = (a_1^\dagger a_1 - a_2^\dagger a_2)/2, \]
\[ \tilde{J} = (a_1^\dagger a_1 + a_2^\dagger a_2)/2, \]

and \(\tilde{H}_0\) contains all (irrelevant) terms which are constant within TPs.

The second step consists of the construction of the classical limit to the problem determined by \(\tilde{H}_{\text{eff}}\). For our case this can be done simply by replacing the quantum operators of the pseudomoments by their quasi-classical counterparts according to

\[ J_x \to L \cos \phi \sin \theta, \]
\[ J_z \to L \cos \theta, \]

where, as usual, the length \(L = J + \frac{1}{2}\) of the classical pseudomomentum is related to \(N\) by \(N + 1 = 2L\) [13].

Omitting \(\tilde{H}_0\), which is unimportant for our purpose, we can write the expression for \(H_{\text{cl}}\) in the form

\[ \frac{H_{\text{cl}}}{2\sqrt{F}a_1} = (s_1 + s_2 L) L \cos \phi \sin \theta + t L^2 \cos^2 \phi \sin^2 \theta + u L^2 \cos^2 \theta. \]

As a third step we have to find all stable stationary points of the classical Hamiltonian function \(H_{\text{cl}}\) obtained in the second step and to investigate their behaviour with increasing \(N\). To understand our interest in stationary points of \(H_{\text{cl}}\) it should be noted that
in classical mechanics each stationary point (maximum and minimum) is surrounded by trajectories localized in its vicinity. Under certain conditions, regular (almost harmonic) sequences of quantum states corresponding to these localized trajectories exist. Thus the information about the stationary points of $H_{cl}$ gives information concerning the existence, the positions and the characteristics (e.g. quasidegeneracies) of the regular sequences of levels in polyads.

In general four types of stationary points are possible. These are listed in table 1 of ref. [13] together with the corresponding values of $H_{cl}$. An energy increase corresponds to an increase of $L$ or $N$. The number and the nature of the stationary points of $H_{cl}$ can change as $L$ passes through certain special values. It is this process (called bifurcation) which is responsible for the rearrangements of the TPs with increasing energy.

Using the theory developed in ref. [13] we see that in our case there are two bifurcation points, at $L= L^*_1=1.32$ and $L= L^*_2=6.01$. The second bifurcation point, $L^*_2$, corresponds to energy values high above the potential barrier and thus it has no physical meaning. The value $L^*_1=1.32$ corresponds to $N=1.64$, i.e. it corresponds to an energy lying between the second and third TP. This energy region is below the potential barrier and thus it has no physical meaning. The value $L^*_1=1.32$ corresponds to $N=1.64$, i.e. it corresponds to an energy lying between the second and third TP. This energy region is below the potential barrier and thus it has no physical meaning. Below this point (for $L < L^*_1$) the TPs are described by the classical Hamiltonian function $H_{cl}$ with two non-degenerate stationary points corresponding to the top and to the bottom of a given TP. In this case the TPs must be of normal type with approximately equidistant level spacings at their top and bottom. For $L > L^*_1$ the minimum of $H_{cl}$ splits into two degenerate minima and one saddle point. The appearance of two degenerate minima gives rise to the formation of the sequence of quasi-degenerate pairs of levels at the bottom of a TP. Note that the structure at the top of the TP does not change.

Thus we see that our qualitative treatment predicts that the higher TPs in propane will show mixed character: the bottom will be described by the local mode model and the top by the normal mode model. The lower TPs have only normal mode character. The transition from the normal mode to the mixed character takes place already in the third TP (see fig. 1). This is the first time that torsional levels have been approximated by an anharmonic oscillator model and treated with this method.

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References