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# Perturbation activated transitions in the high resolution infrared spectrum of C<sub>2</sub>H<sub>6</sub>: rotational constants and torsional splitting in the ground state

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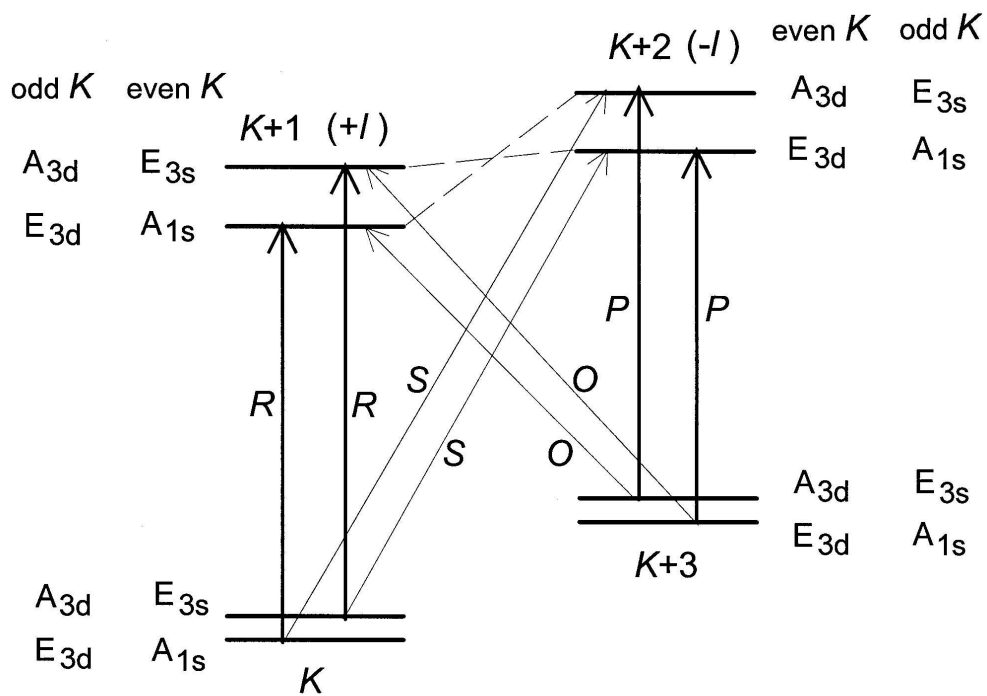


**Perturbation activated transitions in the high resolution infrared spectrum of C<sub>2</sub>H<sub>6</sub>: rotational constants and torsional splitting in the ground state**

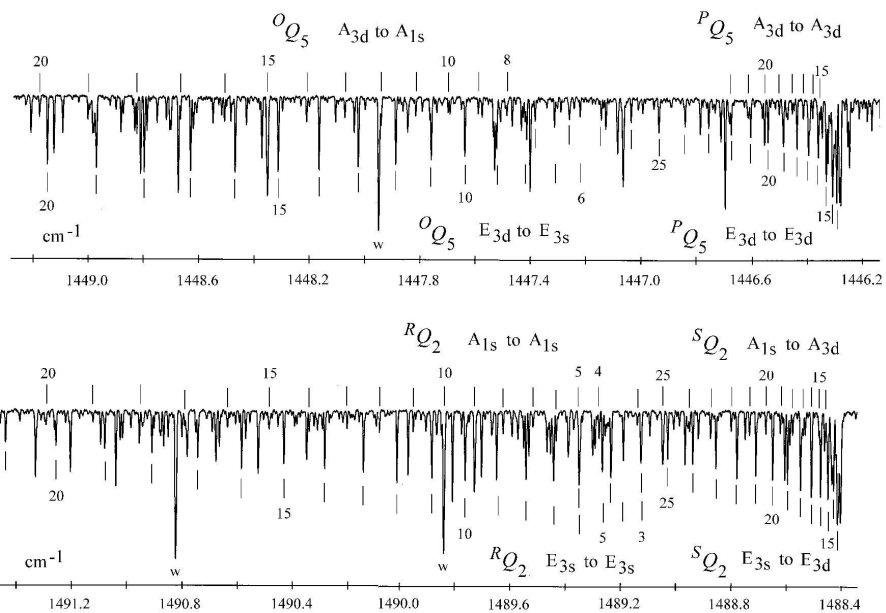
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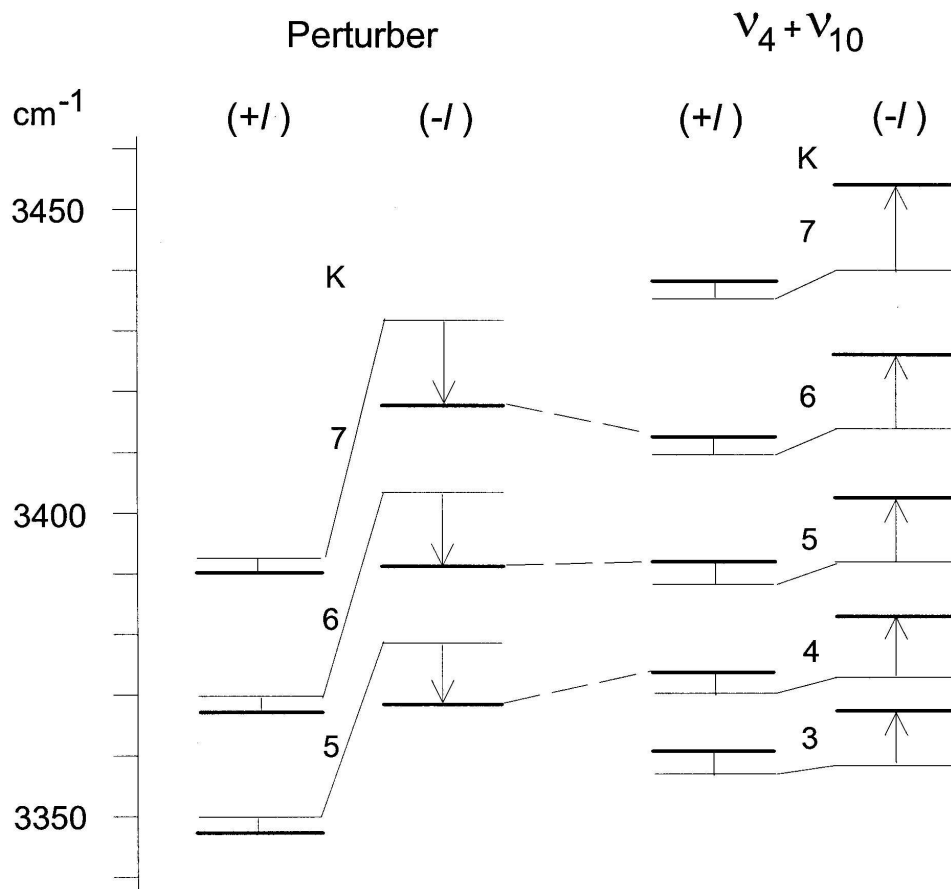


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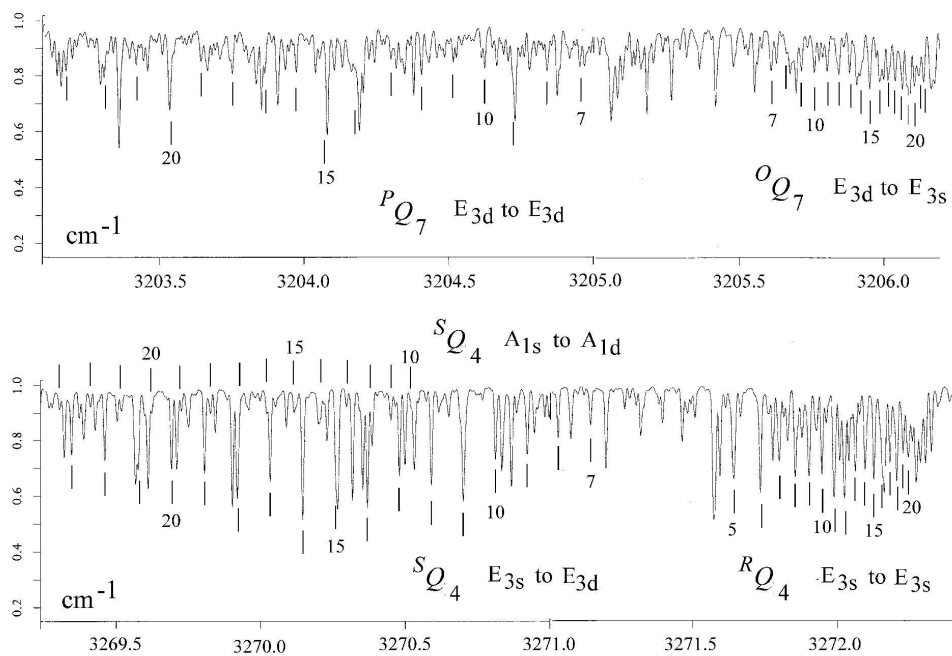


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Perturbation activated transitions in the high resolution infrared spectrum of  $C_2H_6$ :  
rotational constants and torsional splitting in the ground state

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Dedicated to Prof. J. M. Brown on his 65<sup>th</sup> birthday

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## Abstract

The  $l$ -type perturbation mechanisms which activate vibration-rotation transitions with  $\Delta k = \pm 2$ ,  $\Delta(l \text{ modulo } 3) = \mp 1$  in the perpendicular bands of molecules with threefold axial symmetry are investigated in the case of ethane-like molecules. It is shown that in this class of molecules such transitions, combined with the usual ones with  $\Delta k = \Delta(l \text{ modulo } 3) = \pm 1$ , give information not only on the values of the  $K$ -structure rotational parameters, but also on the torsional splitting of the lower combining state. We have examined transitions of this type in two perturbed regions of the infrared spectrum of  $C_2H_6$ , in the  $\nu_8$  fundamental and in the  $\nu_4 + \nu_{10}$  combination. Assuming that the four torsional components in the ground state of  $C_2H_6$  follow the energy pattern generated when tunneling occurs from one minimum of the torsional potential barrier to the two adjacent minima only, we evaluate a torsional splitting of  $0.00566 \pm 0.00015 \text{ cm}^{-1}$  in each rotational level. We can also determine the values of the ground state rotational constants  $A'' = 2.669693 \pm 0.000020 \text{ cm}^{-1}$  and  $10^5 \cdot D_K'' = 0.885 \pm 0.050 \text{ cm}^{-1}$ .



## 1. Introduction

It is well known that rotational components of degenerate vibrational states of molecules with threefold axial symmetry, differing by  $\Delta k = \pm 1$  and  $\Delta l = \mp 2$  (where  $l$  is in general the sum of the  $l_i$ -values of all the excited degenerate modes taken modulo 3, and assumes one of the values 0, -1 or 1) can be coupled by a  $l$ -type interaction, see Ref. [1]. These interactions, often referred to as  $l(2,-1)$ , enhance transitions with  $\Delta k = \pm 2$ , normally vanishingly weak, and these can become detectable in the infrared spectrum, in the resonance regions. Wavenumber differences between pairs of transitions with  $\Delta k = \pm 2$  and  $\Delta k = \mp 1$  sharing the same upper state level depend on the rotational parameters of the lower state, and are normally used to determine the values of the  $k$ -structure rotational constants  $A''$ ,  $D_K''$ , ...

A resonant interaction of this type was observed in the  $\nu_8$  perpendicular fundamental of ethane  $C_2H_6$  [2,3], and the value of the ground state rotational constant  $A''$  was determined [2]. It was assumed that the torsional splitting in the ground state was so small that it could be ignored, and care was not taken to investigate whether pairs of transitions with  $\Delta k = \pm 2$  and  $\Delta k = \mp 1$  reaching the same upper state level originated in the same lower level, or in different torsional components of a vibration-rotation lower level. We can show that such transitions originate in different torsional components of a vibration-rotation level of the lower state, and then their differences also depend on the torsional splitting in that state.

Very recently another  $l(2,-1)$  resonant interaction has been identified in the region of the  $\nu_4 + \nu_{10}$  combination of ethane [4]. Several perturbation enhanced transitions with  $\Delta k = \pm 2$  could be observed, providing further data for the investigation of  $k$ -structure rotational constants and torsional splitting.

In this work we revise the method for determining lower state rotational constants from  $\Delta k = \pm 2$  and  $\Delta k = \mp 1$  transitions, applied to the case of ethane-like molecules, taking the torsional splittings into account. Then we examine the two mentioned  $l(2,-1)$  resonances observed in the infrared spectrum of  $C_2H_6$ , and we determine the values of some rotational and torsional splitting parameters of the ground state.

## 2. $l(2,-1)$ resonance mechanism in ethane-like molecules

We follow the usual notation in which  $K$  is the absolute value of  $k$ , the z-axis total angular momentum quantum number, and  $l$  is the sum of the quantum numbers associated with the vibrational contribution to the z-axis angular momentum in each degenerate mode excited in a given vibrational state. Since  $l$  needs to be defined modulo 3 as far as symmetry is concerned, henceforth we shall assign to this quantum number the value 0, -1 or 1, whichever applies. Obviously, the actual values should be used to evaluate matrix elements, or to find out the operators responsible for interactions.

The  $(+l)$  or  $(-l)$  labels identify vibration-rotation levels in which  $k$  and  $l$ , as defined above, have identical or opposite signs, respectively.

The  $l(2,-1)$  resonance mechanism with activation of transitions with  $\Delta K = \pm 2$  in ethane-like molecules is illustrated in figure 1. The interacting  $(+l)$  and  $(-l)$  upper levels in resonance may belong either to the same vibrational state or to different vibrational states.

Figure 1 about here

One should remember that the partition of a vibration-torsion basis function into vibrational and torsional factors is not univocal when degenerate vibrational states are excited, because torsion dependent factors could be either included in or removed from the degenerate vibrational wavefunctions, see Ref. [5-8]. It is convenient to adopt that form of degenerate vibration basis functions which minimizes the vibration-torsion interaction. In figure 1 the basis degenerate vibrational states are chosen to span the  $E_{1d}$  (or  $E_{2d}$ ) symmetries in the  $G_{36}(EM)$  extended molecular symmetry group, and the torsional symmetries are consistent with this choice. The vibrational torsional quantum number  $v_4$  has the same parity in the interacting states, and the vibration-rotation and torsional factors of the  $l(2,-1)$ -interaction operator in figure 1 are both of  $A_{3d}$  symmetry, see Ref. [6,9]. The correct torsional symmetries in different cases or under different conventions can always be found by the methods shown in tables 2 and 3 of [9]. A misprint occurs in the rightmost column of table 3 of [9], whose heading should be  $\Gamma_{\uparrow} \times \Gamma_{\uparrow}$ . Anyway, symmetry allowed transitions always obey the torsional selection rules  $A \leftrightarrow A$  and  $E \leftrightarrow E$ , as in figure 1. It can easily be shown that the selection rules  $\Delta k = \pm 2$ ,  $\Delta l = \mp 1$  for the interaction matrix elements correspond to  $\Delta K = +1$  from  $(+l)$  to  $(-l)$ , whereas the selection rules  $\Delta k = \Delta l = \pm 1$  (for the usually observable transitions) and  $\Delta k = \pm 2$ ,  $\Delta l = \mp 1$  (for transitions made observable by the interaction near resonance) correspond to  $\Delta K$

= ±1 for normal transitions to (±l) upper levels, and to ΔK = ±2 for the resonance activated transitions to (∓l) upper levels. A special case is represented by the interaction between K=0 and K=1, (-l) levels.

Transitions with ΔK = -2, -1, 1 and 2 are identified by the labels O, P, R and S, as left superscript to the main symbol P, Q or R, which indicate a **shift change** of the main angular momentum quantum number J by -1, 0 and 1 respectively.

In the vibrational ground state of ethane the rotation-torsion energy of the lowest four split torsional components, correlating with the torsional state v<sub>4</sub>=0 in the high barrier limit, are given by

$$E(J,K,\Gamma_\tau) = \nu(\Gamma_\tau) + (A''-B'')K^2 + [B'' - K^2 D_{JK}'' - J(J+1)D_J''] J(J+1) - D_K'' K^4 + \dots \quad (1)$$

The term ν(Γ<sub>τ</sub>) assumes the values ν(A<sub>3d</sub>), ν(E<sub>3s</sub>), ν(E<sub>3d</sub>) and ν(A<sub>1s</sub>), in the order of decreasing energies, accounting for the torsional splitting, see Ref. [5,6]. These values are all close to ν<sub>4</sub>/2, where ν<sub>4</sub> is the value of the harmonic torsional frequency.

In ethane it has been found that centrifugal distortion terms of higher order than those included in equation (1) can be disregarded. Moreover, we assume that the rotational constants have the same values in the four torsional components of the state v<sub>4</sub>=0.

Combining the wavenumbers of transitions with ΔK = ±1 and ΔK = ∓2 (denoted by the appropriate labels R, P, O and S) with the same values of J' and ΔJ, one finds from figure 1 and equation (1):

$$R_K(J)_E - O_{K+3}(J)_E = S_K(J)_E - P_{K+3}(J)_E = -[\nu(E_{3s}) - \nu(E_{3d})] + [(K+3)^2 - K^2]A'' - [(K+3)^4 - K^4]D_K'' - [(K+3)^2 - K^2][B'' - J(J+1)D_{JK}'] + \dots \quad (2)$$

$$R_K(J)_A - O_{K+3}(J)_A = S_K(J)_A - P_{K+3}(J)_A = +[\nu(A_{3d}) - \nu(A_{1s})] + [(K+3)^2 - K^2]A'' - [(K+3)^4 - K^4]D_K'' - [(K+3)^2 - K^2][B'' - J(J+1)D_{JK}'] + \dots \quad (3)$$

The values of rotational constants which determine the J-structure in the lower state, B'', D<sub>J</sub>'', D<sub>JK</sub>'',... are easily determined by combination differences which do not require the observation of perturbation enhanced transitions. Thus the last term in the right hand side of equations (1) (2) and (3) is in general known, and equations differing only by the value of J can differ from each other only because of the errors in the experimental wavenumber data and in the

available values of  $B''$ ,  $D_J''$ ,  $D_{JK}''$ ... Therefore, they all give the same information. Only data obtained for different values of  $K$  provide independent informations, that is independent equations.

In  $C_2H_6$  the nuclear spin statistical weights of E-torsional levels, occurring in equation (2), and those of A-torsional levels, occurring in equation (3), are in the ratio 4:1 for  $K \neq 3n$  and 1:2 for  $K = 3n$ . Therefore if both stronger and weaker transitions are observed for given values of  $K$  and  $J$ , the sum of the splittings  $[\nu(E_{3s}) - \nu(E_{3d})] + [\nu(A_{3d}) - \nu(A_{1s})]$  can be readily evaluated subtracting equation (2) from equation (3). ~~This same result is obtained (within the limits set by the experimental errors) at any value of  $K$ , therefore even if observed data were available for both stronger and weaker transitions at  $n$  different values of  $K$ , the number of independent equations and determinable parameters would be  $n+1$ .~~

### 3. $l(2,-1)$ resonance in the $\nu_8$ band

A  $l(2,-1)$  resonance occurs between the  $K=3,(+l)$  and  $K=4,(-l)$  levels of the  $\nu_8$  vibrational state of  $C_2H_6$ . The resonance of these levels is due to the large upward shift of the  $K=3,(+l)$  level of  $\nu_8$ , caused by a strong interaction (cubic anharmonic in the high-barrier limit and vibration-torsion Coriolis in the low-barrier limit) with  $\nu_4 + \nu_{12}$ . This is shown in detail in figure 8 of [3]. The perturbed transitions originate in the ground state levels with  $K''=2$ , with  $\Delta K=1$  and 2, and  $K''=5$ , with  $\Delta K=-1$  and -2. The  $Q$ -transitions ( $\Delta J = 0$ ) in the affected regions are shown in figure 2.

Figure 2 about here

Transitions involving both torsional components are observed. Although this interaction should follow the scheme of figure 1 with  $K=2$ , the signs of the torsional splittings differ from those predicted from this scheme for two reasons. First, the intrinsic torsional splitting of the  $\nu_8$  state is very small, as in all vibrational states of ethane with  $\nu_4=0$ , and the  $K=3,(+l)$  levels assume the splitting signs typical of the odd values of  $\nu_4$ , being close to resonance with  $\nu_4 + \nu_{12}$ . On the other hand the  $K=4,(-l)$  levels, far from resonance with  $\nu_4 + \nu_{12}$ , assume the splitting pattern of the  $K=3,(+l)$  levels, because of their  $l(2,-1)$ -interaction [3,10]. The result is that the weaker partners (A to A) of the split transition lines always occur at higher wavenumbers than the stronger partners (E to E), see figure 2.

Our analysis relied on a spectrum for which experimental details regarding its recording and measurement and calibration of the  $C_2H_6$  line positions were already described in a previous

contribution [11]. For convenience, they are summarized here. The unapodized spectrum of a mixture of 0.11 mbar of ethane (Praxair, 99.99% purity, 13.8 m absorption path length) and ~0.002 mbar of N<sub>2</sub>O at room temperature was recorded at a resolution of 0.002 cm<sup>-1</sup> in the region from 878 to 1755 cm<sup>-1</sup> using a Bruker IFS120HR Fourier transform spectrometer. The evacuated spectrometer was fitted with a globar source, a 1.3-mm entrance aperture diameter, a KBr beamsplitter, a low-pass optical filter with a cut-off wavenumber at about 2000 cm<sup>-1</sup> and a HgCdTe detector. The line positions were measured by fitting to the observed lines a Voigt profile convolved with an appropriate instrumental line shape function. 68 lines in the ν<sub>3</sub> band of N<sub>2</sub>O from 1246 to 1316 cm<sup>-1</sup> were matched to the reported secondary standards of Maki and Wells [12]. The RMS agreement for the calibrated lines in the N<sub>2</sub>O band was 0.0000074 cm<sup>-1</sup>. Therefore, we estimate that the accuracy of the C<sub>2</sub>H<sub>6</sub> line positions is about 0.00003 cm<sup>-1</sup>.

Therefore we estimate that the accuracy of the calibration line positions is about 0.00003 cm<sup>-1</sup>. Mainly because of the density of the spectrum, the accuracy of the C<sub>2</sub>H<sub>6</sub> line positions should be lower. To estimate it, we compared the calibrated positions of the same lines measured in the spectrum used in this work and 2 spectra recorded at 0.065 and 0.3 mbar, and in otherwise the same experimental conditions. The RMS deviations of the 2 sets of more than 7000 differences were equal to 0.0002 cm<sup>-1</sup> in both cases. We therefore estimate that the accuracy of the C<sub>2</sub>H<sub>6</sub> calibrated line positions is equal to 0.0003 cm<sup>-1</sup>.

These observations allows one to build up the equations (2) and (3), with  $K=2$ .

In order to do this in the best way, we selected sharp and unblended  ${}^R Q_2(J)$  and  ${}^O Q_5(J)$  transition lines which were well related to sharp and unblended  ${}^R R_2(J)$  and  ${}^O P_5(J)$  lines by ground state combination differences. We found 9  ${}^R Q_2(J)$  lines (torsional E<sub>3s</sub> → E<sub>3s</sub>) and 21  ${}^O Q_5(J)$  lines (torsional E<sub>3d</sub> → E<sub>3s</sub>) for the stronger transitions, and 4  ${}^R Q_2(J)$  lines (torsional A<sub>1s</sub> → A<sub>1s</sub>) and 13  ${}^O Q_5(J)$  lines (torsional A<sub>3d</sub> → A<sub>1s</sub>) for the weaker transitions. Similarly, we selected sharp and unblended  ${}^S Q_2(J)$  and  ${}^P Q_5(J)$  transition lines well related to sharp and unblended  ${}^S R_2(J)$  and  ${}^P P_5(J)$  lines by ground state combination differences. We found 12  ${}^S Q_2(J)$  lines and 16  ${}^P Q_5(J)$  lines for the stronger transitions, and 9  ${}^S Q_2(J)$  lines and 5  ${}^P Q_5(J)$  lines for the weaker transitions.

#### 4. $l(2,-1)$ resonance between $\nu_4+\nu_{10}$ and a perturber

The spectral region of the  $\nu_4+\nu_{10}$  combination of ethane, centered at about  $3260\text{ cm}^{-1}$  [4,13], looks very complex, and has not yet been analyzed in detail. Here we refer to the Fourier transform spectrum measured with the Bruker IFS 120 HR Fourier transform spectrometer at the infrared laboratory in the University of Oulu. A tungsten source, KBr beamsplitter and indium antimony (InSb) detector was utilized. The results are combination from two measurements: the pressures and absorption path length being first 260 Pa and 12.8 m and then 93 Pa and 35.2 m, respectively. The total registration time 104 hours gave S/N about 1750 for lines with 100 % absorption. The used instrumental resolution  $0.004\text{ cm}^{-1}$  together with the Doppler width  $0.0051\text{ cm}^{-1}$  gave a line width of  $0.0065\text{ cm}^{-1}$  for small lines. The spectra were calibrated with OCS lines at  $3100\text{ cm}^{-1}$  [12]. Taken into account the uncertainties of the calibration lines, estimated error of the calibration procedure and uncertainty of the used peak positioning method (Optimized Center of Gravity method, Ref. [14]), the accuracy of measured peak positions was estimated to be  $0.00005\text{ cm}^{-1}$  for well separated lines with an average height and width.

The vibrational state  $\nu_4+\nu_{10}$  is expected to interact by cubic anharmonic terms with both  $\nu_4+2\nu_8$  and  $\nu_4+2\nu_{11}$ , containing two quanta of the symmetric ( $\nu_8$ ) and antisymmetric ( $\nu_{11}$ ) combination of the degenerate  $\text{CH}_3$  deformations of the two molecular moieties. It can be shown that the matrix elements for the two anharmonic interactions would be of the same magnitude, if the mentioned deformations of the two methyl groups were uncoupled. In this case it would be simpler to represent the perturber states by the normalized sum and difference of the vibrational wavefunctions of  $\nu_4+2\nu_8$  and  $\nu_4+2\nu_{11}$ , because only one combination would interact with  $\nu_4+\nu_{10}$ . The actual situation is not far from this simple model. The vibrational frequencies  $\nu_8$  and  $\nu_{11}$  differ by about  $4\text{ cm}^{-1}$ , showing that the involved deformations of head and tail are weakly coupled, and in fact it is found that  $\nu_4+\nu_{10}$  is affected by one strong anharmonic interaction with the system  $\nu_4+2\nu_8$  and  $\nu_4+2\nu_{11}$  [4]. This interaction comes to resonance in the  $(-l)$ -side, probably between  $K=7$  and  $K=8$ . The  $K=6,(-l)$  levels of the perturber are pushed down by this interaction, and come to resonance with the  $K=5,(+l)$  levels of  $\nu_4+\nu_{10}$ . This is illustrated in figure 3.

Figure 3 about here

Thus a  $l(2,-1)$  resonance occurs between  $\nu_4+\nu_{10}$  and the perturber, according to the scheme of figure 1 with  $K=4$ , modified to account for the odd value of  $\nu_4$  in the upper states. The  $Q$ -transitions ( $\Delta J=0$ ) affected by this resonance are shown in figure 4.

Figure 4 about here

Unlike the case of the resonance observed in  $\nu_8$ , the transitions with  $\Delta K= -1$  and  $-2$  are markedly weaker than those with  $\Delta K= 1$  and  $2$ . In fact, in a first approximation they are vibrational transitions to a combination of  $\nu_4+2\nu_8$  and  $\nu_4+2\nu_{11}$ , as mentioned, with a transition moment coming mostly from the anharmonic mixing with  $\nu_4+\nu_{10}$ , see figure 3.

Again we selected sharp unblended  $Q(J)$ -transitions well correlating with the associated  $R$  or  $P$  lines, whichever are stronger, by ground state combination differences. We found 8  $^R Q_4(J)$ , 8  $^O Q_7(J)$ , 13  $^R Q_4(J)$ , and 3  $^P Q_7(J)$  good lines for transitions with the higher nuclear spin multiplicity. Only 4 reliable  $^S Q_4(J)$  lines were found by this method for transitions with the lower nuclear spin multiplicity.

## 5. analysis and results

The wavenumber data for the transitions affected by the  $l(2,-1)$  resonance in the  $\nu_8$  band are available for both strong and weak torsional components, and allow one to determine the sum of the torsional splittings  $[\nu(A_{3d})-\nu(A_{1s})]+[\nu(E_{3s})-\nu(E_{3d})]$  in the ground state by combination of the equations (2) and (3), with  $K=2$ . We decided to use in these equations pairs of  $Q$ -transition wavenumber differences with the same value of  $J$ . With this choice the  $J$ -dependent terms disappear in the difference of the two equations, and the value of  $[\nu(A_{3d})-\nu(A_{1s})]+[\nu(E_{3s})-\nu(E_{3d})]$  can be determined without making use of the values of the  $J$ -structure parameters  $B''$ ,  $D_{JK}''$ , ... In this way, the uncertainty on the determined value of this splitting sum is caused only by the errors on the measured transition wavenumbers. Among the wavenumbers selected as described in Section 3, we found for both torsional  $E \rightarrow E$  and  $A \rightarrow A$  transitions two  $^R Q_2(J) - ^O Q_5(J)$  differences, with  $J= 13$  and  $14$ , and two  $^S Q_2(J) - ^P Q_5(J)$  differences, with  $J= 18$  and  $19$ .

Thus four estimated values of the sum of the splittings between the two torsional  $E$ -components and between the two torsional  $A$ -components could be found. We quote the average value,  $[\nu(A_{3d})-\nu(A_{1s})]+[\nu(E_{3s})-\nu(E_{3d})] = 0.011328 \pm 0.000300 \text{ cm}^{-1}$ . The quoted

uncertainty is about the maximum deviation of the four estimated values from the average. It is about ten times found to be equal to the estimated accuracy in the line position in the spectrum of  $\nu_8$ .

Then we consider the data from the  ${}^R Q_4(J) - {}^O Q_7(J)$  and  ${}^S Q_4(J) - {}^P Q_7(J)$  differences, from  $\nu_4 + \nu_{10}$  and its perturber, as described in Section 4. This provides another independent equation (2), with  $K=4$ . With observations at two different values of  $K$ , 2 and 4, and for both torsional  $E \rightarrow E$  and  $A \rightarrow A$  transitions for  $K=2$ , we have 3 independent equations as discussed in Section 2, and we cannot determine the values of the four parameters  $\nu(A_{3d}) - \nu(A_{1s})$ ,  $\nu(E_{3s}) - \nu(E_{3d})$ ,  $A''$  and  $D_K''$ .

In order to evaluate the torsional energies of ethane-like molecules, one may start with a set of high-barrier torsional basis functions centered on six equivalent potential minima disposed on a circle. With this model, if it is assumed that tunneling occurs from one minimum to the two adjacent minima only, and that only basis functions with the same zero-order energy can interact [15,16], the eigenvalues are given by the following expression [5,6]

$$E(\nu_4, \sigma) - E^0(\nu_4) = -2(-1)^{\nu_4} X(\nu_4) \cos \frac{2\pi}{6} \sigma . \quad (4)$$

$E^0(\nu_4)$  is the average vibration-torsion energy and the symbol  $\sigma$  assumes the values 0, 1, 2, 3 for the torsional components  $A_{1s}$  or  $A_{3s}$ ,  $E_{3d}$ ,  $E_{3s}$ , and  $A_{3d}$  or  $A_{1d}$ . The torsional components  $A_{1s}$  and  $A_{3d}$  occur with the even values of  $\nu_4$ , and the torsional components  $A_{1d}$  and  $A_{3s}$  occur with the odd values of  $\nu_4$ .

The lowest torsional levels, belonging to the torsional ground state ( $\nu_4=0$ ), are those which follow equation (4) most closely.

Equation (4) shows that for  $\nu_4=0$  the torsional components  $A_{1s}$ ,  $E_{3d}$ ,  $E_{3s}$ , and  $A_{3d}$  are shifted by  $-2X''$ ,  $-X''$ ,  $X''$  and  $2X''$  respectively with respect to the average value  $E^0(\nu_4=0)$ , with  $X'' = X(\nu_4=0)$ . Therefore,  $\nu(E_{3s}) - \nu(E_{3d}) = 2X''$ ,  $\nu(A_{3d}) - \nu(A_{1s}) = 4X''$ , and  $[\nu(E_{3s}) - \nu(E_{3d})] + [\nu(A_{3d}) - \nu(A_{1s})] = 6X''$ . The splittings of the torsional components of a given rotational state, that is  $\nu(E_{3s}) - \nu(A_{1s})$  for even  $K''$  and  $\nu(A_{3d}) - \nu(E_{3d})$  for odd  $K''$ , are  $3X''$ . In the approximation of equation (4), we find for  $C_2H_6$  that  $X'' = 0.01888 \pm 0.00005 \text{ cm}^{-1}$ , and the torsional splittings in given rotational states of the ground state are  $3X'' = 0.00566 \pm 0.00015 \text{ cm}^{-1}$ .

Now we can use Equation (2) with  $\nu(E_{3s}) - \nu(E_{3d}) = 2X'' = 0.03776 \text{ cm}^{-1}$ , with  $K=2$  and the data from  $\nu_8$  and  $K=4$  and the data from  $\nu_4 + \nu_{10}$  and its perturber.



From  $\nu_8$  we found four pairs of good transitions data with the same  $J$ -value:  ${}^R Q(J)$  and  ${}^O Q(J)$  with  $J=13$  and  $14$ , and  ${}^S Q(J)$  and  ${}^P Q(J)$  with  $J=18$  and  $19$ . Thus, handling the  $J$ -dependent terms of equation (2) by means of the values of  $B''$  and  $D_{JK}''$  already known [17], we found four expression for the first equation in  $A''$  and  $D_K''$ , with  $K=2$ .

For  $\nu_4+\nu_{10}$  we also found four expressions for the second equation, with  $K=4$ , from good pairs of  ${}^S Q(J)$  and  ${}^P Q(J)$  transitions with  $J=10$  and  $12$  and  ${}^R Q(J)$  and  ${}^O Q(J)$  transitions with  $J=13$  and  $15$ . In this way we could build up the system of equations for the determination of  $A''$  and  $D_K''$  in 16 different ways. The average values determined for these parameters are  $A'' = 2.669693 \pm 0.000020 \text{ cm}^{-1}$  and  $D_K'' = 0.885 \cdot 10^{-5} \pm 0.050 \cdot 10^{-5} \text{ cm}^{-1}$ . The quoted uncertainty in each determined value is a rounded value of the maximum deviation of the 16 determined values from their average.

The determined parameter values are reported in table 1, and the data used in their evaluation are reported in table 2.

Table 1 about here

Table 2 about here

The determined value of  $D_K''$ ,  $0.885 \cdot 10^{-5} \text{ cm}^{-1}$ , is closer to the value from the force field of Duncan et al. [19],  $0.944 \cdot 10^{-5} \text{ cm}^{-1}$ , than to that of Nakagawa and Shimanouchi [20],  $1.09 \cdot 10^{-5} \text{ cm}^{-1}$ . The uncertainty on the determined value of  $3X''$  due to the deviations of the actual torsional splitting pattern from the approximate model of Equation (4), for the ground state of ethane, is probably comparable with the value quoted in table 2. The improvement in the determined value of  $A''$  with respect to Ref. [2] is mostly due to the account for the torsional splitting in the ground state, even if with the help of an approximate model. The predicted torsional splitting in a given rotational level of the ground state,  $\nu(E_{3s})-\nu(A_{1s})$  for the even values of  $K''$  and  $\nu(A_{3d})-\nu(E_{3d})$  for the odd values of  $K''$ ,  $0.00566 \text{ cm}^{-1}$ , is in good agreement with calculations from estimated barrier potential terms [21,22]. Susskind et al. [21] report a splitting of  $0.00540 \text{ cm}^{-1}$  in the ground state of  $C_2H_6$ .

We also tried to determine the values of  $A''$ ,  $\nu(E_{3s})-\nu(E_{3d})$  and  $\nu(A_{3d})-\nu(A_{1s})$ , with  $D_K''$  fixed at the value predicted by the force field of Duncan et al. [19], but the calculated value of  $\nu(A_{3d})-\nu(A_{1s})$  was markedly lower than two times the value of  $\nu(E_{3s})-\nu(E_{3d})$ , with an unrealistic deviation from the model leading to equation (4). This provides further evidence that the value of  $D_K''$  must be lower than  $0.944 \cdot 10^{-5} \text{ cm}^{-1}$ .

## 6. conclusions

We have shown that in ethane-like molecules the observation of transitions with  $\Delta K = \pm 2$ , enhanced by  $l(2,-1)$  resonances, provides also information on the torsional splittings in the lower state. In this work we have been able to determine the value of the sum of the splittings  $\nu(E_{3s})-\nu(E_{3d})$  and  $\nu(A_{3d})-\nu(A_{1s})$  in the ground state of  $C_2H_6$ , but these two splittings can be determined separately, if enough data are available. It is unfortunate that these are not the splittings occurring in a given rotational level of the ground state, and then more directly related to the splittings of the spectral lines, since each rotational level contains one A and one E torsional components, with splittings  $\nu(E_{3s})-\nu(A_{1s})$  for the even values of  $K''$  and  $\nu(A_{3d})-\nu(E_{3d})$  for the odd values of  $K''$ .

The neglect of torsional splitting terms in Equations (2) and (3) does also affect the determination of the values of the rotational constants  $A''$ ,  $D_K''$ ..., therefore if torsional splittings cannot be determined, the use of even approximate estimated values can substantively improve the determination of these rotational constants.

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## References

- [1] M. L. Grenier-Besson, *J. Physique* **21**, 555 (1960).
- [2] F. Lattanzi, C. di Lauro, and N. Legay-Sommaire, *J. Mol. Spectrosc.* **156**, 237 (1992).
- [3] M. Hepp and M. Herman, *J. Mol. Spectrosc.* **194**, 87 (1999).
- [4] F. Lattanzi, C. di Lauro, and V.-M. Horneman, work in progress.
- [5] J. Susskind, *J. Mol. Spectrosc.*, **49**, 1 (1974).
- [6] J. T. Hougen, *J. Mol. Spectrosc.* **82**, 260 (1980).
- [7] P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy*, 2<sup>nd</sup> ed. (NRC Research Press, Ottawa, 1998).
- [8] C. di Lauro and F. Lattanzi, *J. Mol. Spectrosc.* **162**, 375 (1993).
- [9] C. di Lauro, F. Lattanzi, and A. Valentin, *Mol. Phys.* **89**, 663 (1996).
- [10] F. Lattanzi, C. di Lauro, and N. Legay-Sommaire, *J. Mol. Spectrosc.* **156**, 227 (1992).
- [11] F. Lattanzi, C. di Lauro, M. Herman, and J. Vander Auwera, *J. Mol. Spectrosc.* **216**, 308 (2002).
- [12] A. G. Maki and J. S. Wells, *Wavenumber Calibration Tables From Heterodyne Frequency Measurements* (NIST Special Publication 821, U.S. Government Printing Office, Washington D.C. 1991).  
(Data updated in November 1994 and available on the web site of the Physics Laboratory of the National Institute of Standards and Technology, <http://physics.nist.gov>).
- [13] M. Hepp, and M. Herman, *J. Mol. Spectrosc.* **197**, 56 (1999).
- [14] V.-M. Horneman, *Acta Univ. Oul.* **A239**, 57 (1992).
- [15] W. G. Harter and C. W. Patterson, *J. Chem. Phys.* **66**, 4872 (1977).
- [16] R. P. Feynman, R. B. Leighton, and M. Sands, *Lectures on Physics*, I-19-4 III,13-1,2 (Addison Wesley, Reading Mass., 1963).
- [17] L. Henry, A. Valentin, W. J. Lafferty, J. T. Hougen, V. Malathy Devi, P.P. Das, and K. Narahari Rao, *J. Mol. Spectrosc.* **100**, 260 (1983).
- [18] D. W. Lepard, D. E. Shaw, and H. L. Welsh, *Can. J. Phys.* **44**, 2353 (1966)
- [19] J. L. Duncan, R. A. Kelly, G. D. Nivellini, and F. Tullini, *J. Mol. Spectrosc.* **98**, 87 (1983).
- [20] I. Nakagawa and T. Shimanouchi, *J. Mol. Spectrosc.* **39**, 255 (1971).

[21] J. Susskind, L. Iredell, W. E. Blass, D. C. Reuter, G. W. Halsey, and D. E. Jennings, *J. Mol. Spectrosc.* **192**, 119 (1998).

[22] N. Moazzen-Ahmadi, *J. Mol. Spectrosc.* **214**, 144 (2002).

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**Legends of Tables**

- 1- Ground state rotational and torsional parameters of  $C_2H_6$ . Numbers in parentheses are uncertainties in units of the last quoted digit. See text.
- 2-  $Q$ -transition wavenumbers in  $cm^{-1}$  used in our calculations, and wavenumbers of their associated  $R$  or  $P$ -transitions occurring to the same upper level. The torsional symmetries of the combining levels are also shown. Transitions with  $K''=2$  and  $5$  occur to the  $\nu_8$  vibrational upper state, and those with  $K''=4$  and  $7$  occur to the  $\nu_4+\nu_{10}$  vibrational upper state and its main perturber. See text.

## Legends of Figures

- 1-  $l(2,-1)$  resonance between  $(+l)$  and  $(-l)$  levels of degenerate vibrational states of a molecule like ethane. The interacting levels are connected by broken lines. Transitions with  $\Delta K = \pm 1$  are represented by thick arrowed lines. Perturbation enhanced transitions with  $\Delta K = \pm 2$  are represented by narrow arrowed lines. The torsional symmetries of the levels, shown for both even and odd values of  $K$ , are consistent with a vibration-torsion basis factorization in which the degenerate vibrational states span  $E_{1d}$  or  $E_{2d}$  symmetry, and apply to the case of even values of  $\nu_4$  in all states. For odd values of  $\nu_4$  the sign of the splitting in each A,E torsional doublet has to be inverted, and the species  $A_{1s}$  and  $A_{3d}$  must be replaced by  $A_{3s}$  and  $A_{1d}$ , respectively.
- 2- Effects of the  $l(2,-1)$  resonance between the  $K=3,(+l)$  and  $K=4,(-l)$  levels of  $\nu_8$  of  $C_2H_6$ , in the regions of their  $Q$ -branches. Different transitions to common upper levels form quite similar patterns.
- 3- Perturbation mechanism causing the resonance between the levels  $K=5,(+l)$  of  $\nu_4+\nu_{10}$  and  $K=6,(-l)$  of a perturber in  $C_2H_6$ . The strong cubic anharmonic resonance between the  $(-l)$  levels of the two vibrational states causes large energy shifts, represented by arrowed lines. See text.
- 4- Effects of the  $l(2,-1)$  resonance between the  $K=5,(+l)$  levels of  $\nu_4+\nu_{10}$  and the  $K=6,(-l)$  levels of a perturber, in the regions of their  $Q$ -branches. Different transitions to common upper levels form quite similar patterns. See text.

Table 1

	This work	Ref. [17]	Ref. [2]	Ref. [18]
$A''/\text{cm}^{-1}$	2.669693 (20)		2.66952 (4)	2.671
$B''/\text{cm}^{-1}$		0.66302901 (39)		
$D_K''/10^{-5}\text{cm}^{-1}$	0.885 (50)			
$D_J''/10^{-5}\text{cm}^{-1}$		0.103174 (24)		
$D_{JK}''/10^{-5}\text{cm}^{-1}$		0.26604 (35)		
$3X''/\text{cm}^{-1}$	0.00566 (15)			
$[\nu(E_{3s})-\nu(E_{3d}) + \nu(A_{3d})-\nu(A_{1s})]/\text{cm}^{-1}$	0.011328 (300)			

Table 2

${}^R Q_2$		${}^R R_2$		${}^R Q_4$	${}^R R_4$				
$J$	$E_{3s} \rightarrow E_{3s}$	$A_{1s} \rightarrow A_{1s}$	$J$	$E_{3s} \rightarrow E_{3s}$	$A_{1s} \rightarrow A_{1s}$	$J$	$E_{3s} \rightarrow E_{3s}$	$J$	$E_{3s} \rightarrow E_{3s}$
13	1490.14646	1490.20678	12	1507.37567	1507.43561	13	3272.06181	12	3289.29096
14	1490.28701	1490.34372	13	1508.84022	1508.89680	15	3272.12603	14	3292.00194
${}^O Q_5$		${}^O P_5$		${}^O Q_7$	${}^O P_7$				
$J$	$E_{3d} \rightarrow E_{3s}$	$A_{3d} \rightarrow A_{1s}$	$J$	$E_{3d} \rightarrow E_{3s}$	$A_{3d} \rightarrow A_{1s}$	$J$	$E_{3d} \rightarrow E_{3s}$	$J$	$E_{3d} \rightarrow E_{3s}$
13	1448.02594	1448.07489	14	1429.47431	1429.52377	13	3205.88042	14	3187.33044
14	1448.16799	1448.21358	15	1428.29306	1428.33860	15	3205.95018	16	3184.75458
${}^S Q_2$		${}^S R_2$		${}^S Q_4$	${}^S R_4$				
$J$	$E_{3s} \rightarrow E_{3d}$	$A_{1s} \rightarrow A_{3d}$	$J$	$E_{3s} \rightarrow E_{3d}$	$A_{1s} \rightarrow A_{3d}$	$J$	$E_{3s} \rightarrow E_{3d}$	$J$	$E_{3s} \rightarrow E_{3d}$
18	1488.55120	1488.57978	17	1512.39578	1512.42484	10	3270.81020	9	3284.06526
19	1488.59794	1488.62496	18	1513.76440	1513.79196	12	3270.58945	11	3286.49469
${}^P Q_5$		${}^P P_5$		${}^P Q_7$	${}^P P_7$				
$J$	$E_{3d} \rightarrow E_{3d}$	$A_{3d} \rightarrow A_{3d}$	$J$	$E_{3d} \rightarrow E_{3d}$	$A_{3d} \rightarrow A_{3d}$	$J$	$E_{3d} \rightarrow E_{3d}$	$J$	$E_{3d} \rightarrow E_{3d}$
18	1446.43953	1446.45693	19	1421.27531	1421.29273	10	3204.62339	11	3190.04489
19	1446.48850	1446.50388	20	1420.00345	1420.01917	12	3204.40544	13	3187.17977



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