Intensities and Widths of the Rovibrational Lines Observed in the $2\nu_5$ Overtone Band of Cyanoacetylene

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The relative intensities and Lorentz half-widths of rovibrational transitions observed for the $2\nu_5$ overtone band of cyanoacetylene, HCCCN, have been determined. The line widths and the intensities were obtained by fitting the observed line profiles with Voigt functions. The Lorentz half-width shows a clear J dependence and vanishes at $J \sim 100$. In the intensity calculation, we took into account the effects of the accidental resonances between the $v_5 = 2$ state and the $(v_4 = 1, v_7 = 2)$ state as well as those of the generic ℓ-type resonance. Peak intensities have been found not to be the appropriate presentation of the line intensity because of the strong J dependence of the half-width.

1. Introduction

In a previous paper [1] we have reported a detailed analysis of the $2\nu_5$ band system of cyanoacetylene, HCCCN, observed by the high resolution Fourier transform infrared (FTIR) spectrometer, BRUKER IFS-120, at Wuppertal. In the course of that work, we found strong intensity perturbations due to the accidental anharmonic resonance between the $v_5 = 2$ state and the $(v_4 = 1, v_7 = 2)$ state, where the mode ν_4 is the lowest stretching vibration. Stimulated by this observation, an intensity analysis has been carried out for the $2\nu_5$ band in order to present an appropriate procedure for the intensity determination of rovibrational lines of polyatomic linear molecules. Cyanoacetylene is a good candidate for this purpose, because previous spectroscopic studies (for references see those given in [1]) indicate that the molecule is fairly rigid and can be considered as a textbook example.

In our laboratory in Cologne, we have developed a procedure based on computer programs for analyzing absorption line profiles in relation to high precision studies of pressure effects on rovibrational lines observed by diode laser spectrometers [2] and FTIR spectrometers [3]. We have applied this line shape analysis procedure in the present study which has allowed us to determine precisely the line-profile parameters not only for an isolated line but also for lines overlapping each other.

As presented in [4–6], ℓ-type resonances perturb the rovibrational line intensities. In addition to the effect of those ℓ-type interactions generic for linear molecules, the intensity perturbation due to accidental resonances mentioned above has been properly analyzed.

The experimental procedure and the interaction analyses are given in [1] and we kept the same notations here for the theoretical expressions.

2. Line Profile Analysis

A typical result of the line profile analysis is presented in Figure 1. The expression

$$\tau_i(\nu) = p\, l\, S_i\, f_V^{(i)}(\nu, \nu_i) \tag{1}$$

gives the optical depth, $\tau_i(\nu)$, at a given frequency ν caused by the i-th line; $f_V^{(i)}$ is the Voigt profile function for the i-th line, p the pressure of the sample gas l the optical path length, and S_i is its integrated absorption coefficient, with the assumption that the integral of the Voigt profile function is normalized to unity [7]. The procedure for calculating the Voigt functions is presented in detail in [2, 3].

In cases where plural lines are overlapping each other, as in most cases in the present work, the calculated optical depths for each line are added together:

$$\tau(\nu) = \sum_i \tau_i(\nu) . \tag{2}$$

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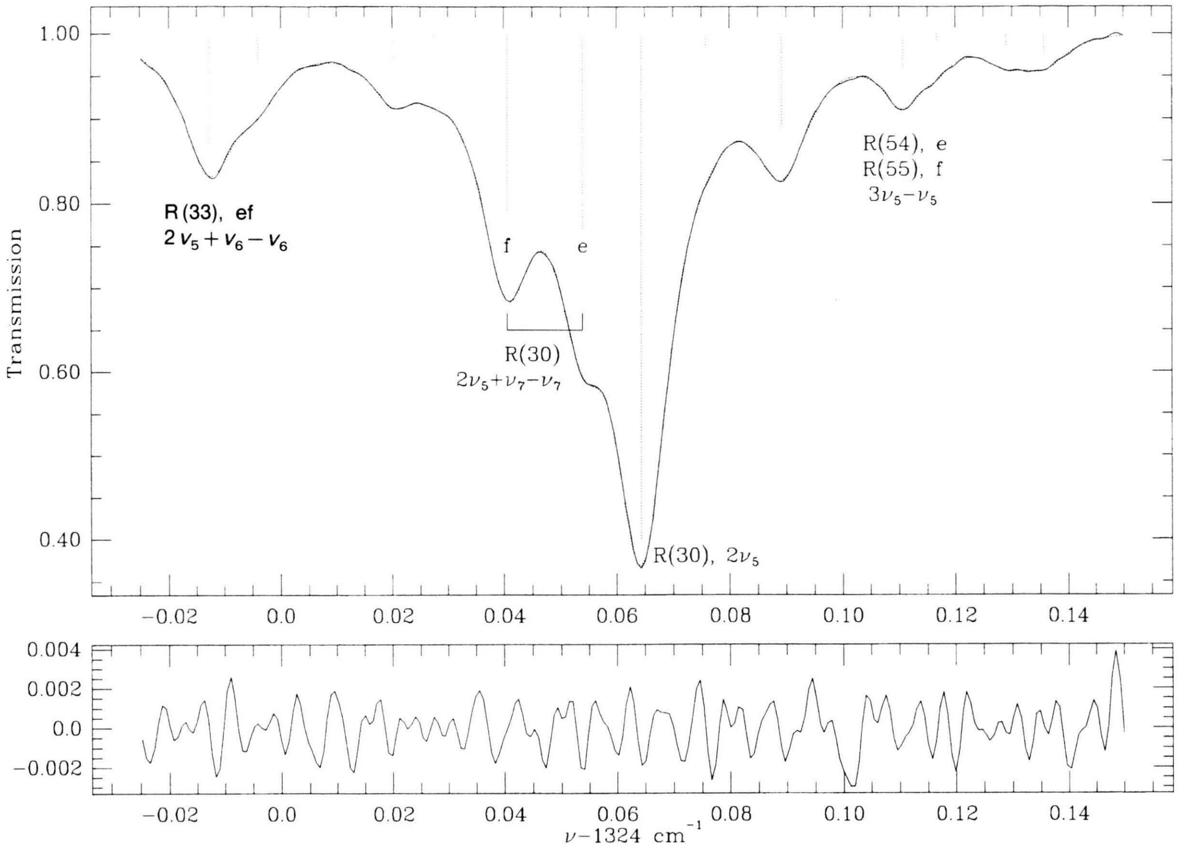

Fig. 1. The observed and calculated spectrum near 1324 cm^{-1}, where we found 13 overlapping lines; among them five lines have been identified in the present work as indicated. The unidentified lines may belong to some hot bands from the $v_7 \geq 2$ states. The solid curve represents the observed spectrum, and the dotted line represents the calculated one which can hardly be seen in this plot because both curves agree so well. The observed(solid)–calculated(dotted) values are plotted at the bottom in an expanded scale; no systematic deviation can be seen.

The calculated optical depth $\tau(\nu)$ is then used to calculate the transmission spectrum

$$T(\nu) = \exp[-\tau(\nu)]. \tag{3}$$

Small corrections for the background curve

$$I_0(\nu) = c_0 + c_1\nu + c_2\nu^2 \tag{4}$$

had to be introduced although they were very close to unity, because the experimental spectrum was not a true transmission spectrum, but it was obtained by dividing the sample spectrum by the spectrum of the empty cell. The latter was measured in low resolution in order to obtain a smooth background curve.

The calculated transmission curve was then fitted to the observed one by adjusting the intensity $p\,l\,S_i$, the line position ν_i, the Lorentz width $\gamma_L^{(i)}$ (HWHM), and some background parameters. The Doppler width γ_D (HWHM) of the molecule, ~ 0.0013 cm^{-1} at room temperature in this frequency range, was fixed at its theoretical value.

Although the instrumental line width, which is expected to be ~ 0.0015 cm^{-1} (HWHM), was neglected in the present analysis, we could fit the line profiles satisfactorily, as shown in Figure 1. The residual of the fit shown in this figure is about ± 0.002 in the transmission scale without any systematic deviation.

The Lorentz widths γ_L extracted from the observed spectrum are displayed in Fig. 2 as functions of the lower state J quantum number. This plot suggests that the resolution is limited by pressure broadening for most of the observed lines. The observed Lorentz width increases with J in the low J region and de-

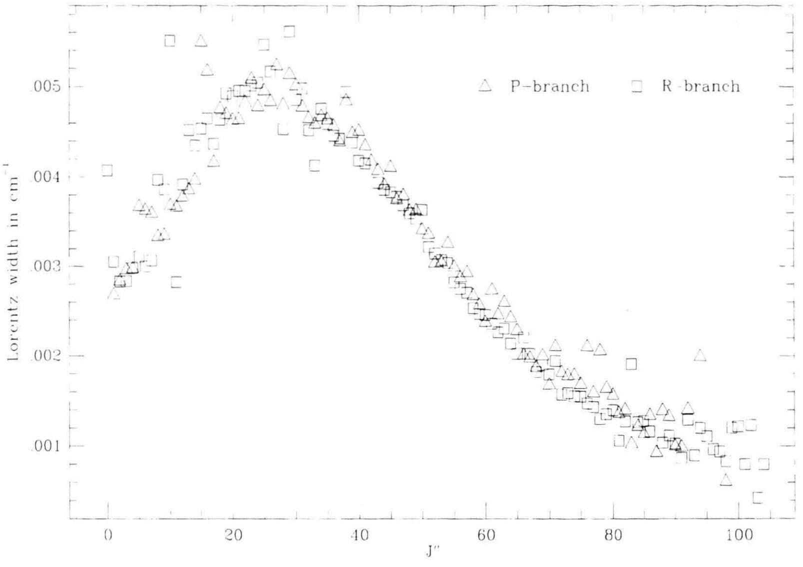

Fig. 2. The Lorentz widths γ_L extracted from the observed spectrum of the $2\nu_5$ band are illustrated as functions of the lower state J quantum number. The triangle (△) represents the P-branch transitions and the square (□) the R-branch transitions. The lower limit of ~ 0.001 cm^{-1} is due to the contribution of the instrumental shape function (see text).

creases in the high J region. The width seems to converge to a lower limit of $\sim$ 0.001 cm^{-1} at high J. We suppose that this lower limit represents the contribution of the instrumental width which was neglected in the analysis.

3. Observed Line Intensities

Since the line width depends strongly on J, the peak intensity does not represent the true intensity of the individual rovibrational line. Only the integrated intensities obtained from the line profile analysis described in the previous section can give the correct values. The obtained integrated intensity $p\,l\,S_m$ in units of cm^{-1} is plotted in Fig. 3 as a function of m, which is $-J$ for the $P(J)$ transitions and $J \pm 1$ for $R(J)$.

The integrated absorption coefficient S_i in (1) is formulated as [7]

$$S_i^f = (8\pi^3/3hc)(n/Q)\,\nu_{if}\exp(-hcE_i/k_B T) \quad (5)$$
$$\times\,[1-\exp(-hc\nu_{if}/k_B T)]\,|\langle i|\mu|f\rangle|^2,$$

where the i-th transition is now assigned to $f \leftarrow i$, ν_{if} is the transition wavenumber (cm^{-1}), E_i the lower state energy (cm^{-1}), Q the total partition function, n the number of molecules per unit volume at unit pressure, and μ the transition dipole moment. In the case of no rovibrational interaction, we can rewrite the transition intensities of a linear molecule, (5), with the Hönl-London factor A_{KJ} [8], a vibrational factor f_v, and a degeneracy factor g_i for the lower state as

$$S_i^f = (8\pi^3/3hc)(n/Q)\,\nu_{if}\,g_i\exp(-hcE_i/k_B T)$$
$$\times\,[1-\exp(-hc\nu_{if}/k_B T)]\,|\mu|^2 f_v A_{KJ}\,, \quad (6)$$

where the state i is represented by the two quantum numbers, J and $K = |k|$ in the Hönl-London factor. For calculating the vibrational factor, the relation

$$k = l_5 + l_6 + l_7 \quad (7)$$

should be kept in mind. Considering that $hc\nu_{if} \gg k_B T$ in the present case, we obtain an approximate equation

$$p\,l\,S_i^f \approx C(2J+1)\,\nu_{if}\exp(-hcE_i/k_B T)\,f_v A_{KJ}\,, \quad (8)$$

where the dimensionless factor C depends on the temperature T, the size of the transition dipole moment, and the column density of the sample molecule.

In the case of a resonance system, which is always the case for linear molecules with an excited bending mode because of the generic ℓ-type interactions, the line strength $|\langle i|\mu|f\rangle|^2$ should be evaluated on the basis of the perturbed wavefunctions as discussed in [4–6]. For the present case, the perturbed wavefunction of the $(0, 2, 0, 0)^{0+}$ state is given as

$$\begin{aligned}|0, 2(0), 0(0), 0(0);\, J, 0+\rangle^p &= a\,|0, 2(0), 0(0), 0(0);\, J, 0+\rangle \\ &+ b\,|0, 2(2), 0(0), 0(0);\, J, 2+\rangle \\ &+ c\,|1, 0(0), 0(0), 2(0);\, J, 0+\rangle \\ &+ d\,|1, 0(0), 0(0), 2(2);\, J, 2+\rangle\,. \end{aligned} \quad (9)$$

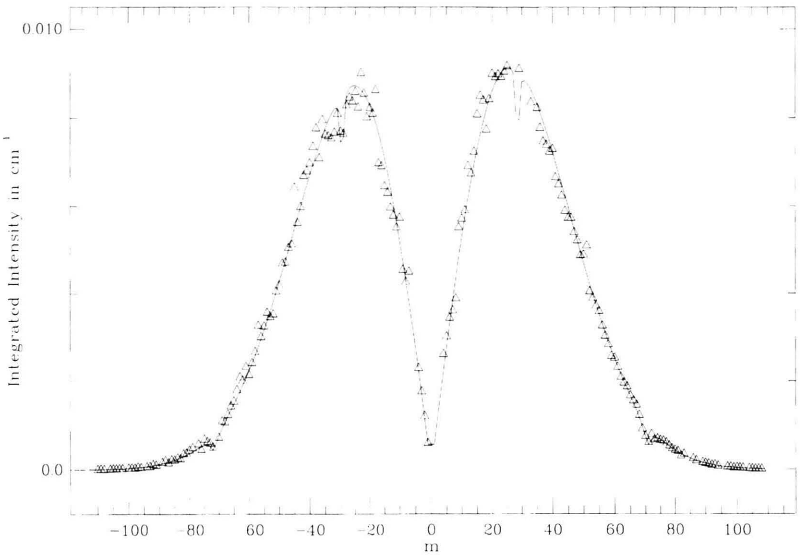

Fig. 3. The observed integrated intensity $p\,l\,S_m$ is plotted against *m*, which is $-J$ for the transition $P(J)$ and $J+1$ for $R(J)$. The triangles (△) represent the experimental values and the solid line represents the calculated ones.

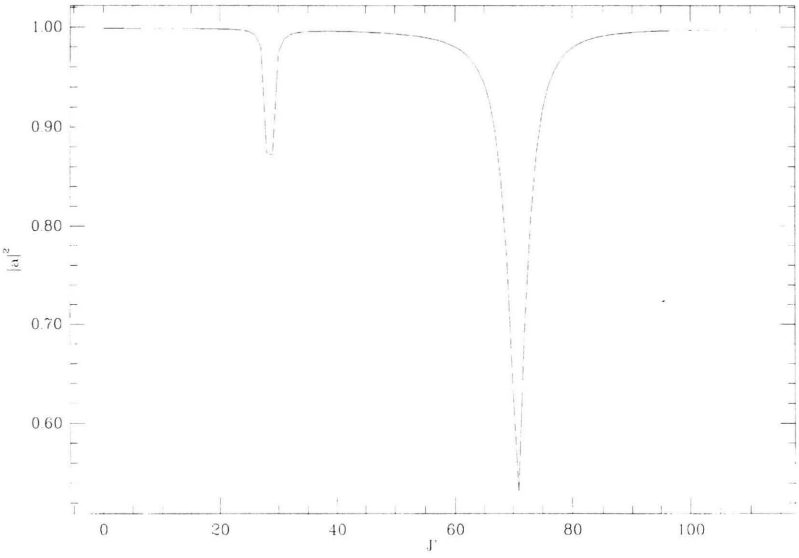

Fig. 4. The square of the mixing coefficient *a* of (9) is plotted against the J' quantum number. The sharp decrease of the values at $J' \sim 28$ and 71 are due to the accidental resonances [1] and the occurrence of strong mixing.

Since the transitions from the ground state to the three perturber levels are all vanishingly weak, the line strength of the perturbed $2\nu_5$ band depends solely on the mixing coefficient *a* and the unperturbed line strength of the $2\nu_5$ band;

$$\begin{aligned} &|\langle 0, 0(0), 0(0), 0(0);\ J'', 0 \\ &+ |\mu| 0, 2(0), 0(0), 0(0);\ J', 0+\rangle^p|^2 \\ &\quad = a^2 |\langle 0, 0(0), 0(0), 0(0);\ J'', 0 \\ &\qquad + |\mu| 0, 2(0), 0(0), 0(0);\ J', 0+\rangle|^2 . \end{aligned} \tag{10}$$

Since the coefficient *a* for each *J* has been determined by the line position analysis [1], the line strength can be readily calculated except for the size of the transition moment $|\mu|$.

In the present analysis we have adjusted two parameters, the parameter *C* in (8) and the temperature *T*, to reproduce the observed integrated intensities. As displayed in Fig. 3, the calculated intensities agree very well with those obtained experimentally. Some discrepancies can be seen in the figure, which are mainly caused by the difficulties in the line shape analysis in cases of heavy overlapping of absorption lines. The temperature has been determined to be 297(2) K. This value is very close to the temperature measured at the spectrometer (298 K), and thus indicates the high reliability of the present analysis. The dimensionless parameter C has been determined to be $4.3218(26) \times 10^{-7}$, also with very high precision.

4. Discussion

As shown in Fig. 3, the calculated integrated intensities of the $2\nu_5$ rovibrational lines reproduce the observed ones very well without introducing the Herman-Wallis factor [9]. The observed intensity anomalies due to the accidental resonances at $J' \sim 28$ and 71 [1] are also reproduced very satisfactorily by the present calculation. Figure 4 displays the square of the mixing coefficient a of (9). The intensity perturbations are caused dominantly by the accidental resonances. The contribution of the ℓ-type resonance in the $v_5 = 2$ state is very small.

In conclusion, the line widths have been observed to depend strongly on J, showing a significant contribution of pressure broadening effect; in such cases, the integrated line intensities have to be used for the measurements of the line strength instead of the peak intensities. By fitting the absorption line profile we were able to determined the integrated intensities very accurately, even for lines overlapped with other lines. Unfortunately the partial pressure of the sample in the cell was not precisely known, some impurity contamination having been detected in the recorded spectrum, and therefore a further quantitative discussion is not useful in the present work.

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