

# High resolution spectroscopy of several rovibronically excited bands of 5-cyanoindole – The effect of vibrational averaging

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## ARTICLE INFO

### Article history:

Available online 5 December 2012

### Keywords:

Electronic spectroscopy  
Rotational resolution  
5-Cyanoindole  
Vibronic coupling  
Vibrational averaging

## ABSTRACT

The rovibronic spectra of two bands of 5-cyanoindole at 348 and 884  $\text{cm}^{-1}$  have been measured and analyzed using a rigid rotor Hamiltonian. A vibrational assignment could be given on the basis of an anharmonic analysis of the vibrational spectrum of 5-cyanoindole making use of the information of the vibrationally averaged rotational constants. Strong vibronic mixing to a higher lying electronically excited state has been found.

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## 1. Introduction

The photophysics and photochemistry of indole and substituted indoles is governed by the existence of two electronically excited singlet states, which are labeled  $^1L_a$  and  $^1L_b$  following the nomenclature of Platt for catacondensed aromatics [1]. Depending on the substituent the energy difference between these two states differs largely, in some cases even their energetic order is reversed. Vibronic spectroscopy with rotational resolution provides an elegant approach to the nature of the excited states via determination of the transition dipole moment directions.

For indole it is generally accepted now, that the lowest electronically excited singlet state of indole is a state with  $L_b$  character, followed by an  $L_a$  like state, approximately 1400  $\text{cm}^{-1}$  higher in energy [2–7]. This has been shown by quantum chemical calculations [2,5] from the theory side and by two-photon-induced fluorescence anisotropy measurements [3], two-photon excitation spectroscopy [4], linear dichroism measurements on partially oriented indole in stretched polyethylene films [8], and by rotationally resolved spectroscopy of vibronic bands of indole [6,7].

The introduction of substituents in different positions of the chromophore may change this energetic separation of the two states and sometimes even reverse them. For 5-methoxyindole the  $^1L_a$  state is predicted to lie more than 4000  $\text{cm}^{-1}$  above the  $^1L_b$  state, one of the largest gaps in the indole row [9]. For isolated tetrahydrocarbazole, on the other hand, it could be shown that the lowest excited singlet state is the  $^1L_a$  state [10], while for 2,3-dimethylindole the energy order critically depends on the local

surrounding of the chromophore. Even a small perturbation like an argon matrix as local surrounding shifts the  $^1L_a$  state below the  $^1L_b$ , with a reversed order in gas phase [11–13]. In gas phase the spectral position and lifetime of the electronic origin of 5CI were determined by Huang and Sulkes using time-correlated single photon counting for  $S_1$  levels in supersonic free jet expansions [14]. The rotationally resolved spectrum of the electronic origin was measured and analyzed by Oeltermann et al. [15].

In the present publication we show, how the information of vibrationally averaged rotational constants can be utilized for a straightforward assignment of rovibronic spectra.

## 2. Techniques

### 2.1. Experimental procedures

5CI ( $\geq 98\%$ ) was purchased from Activate Scientific and used without further purification. The experimental set up for the rotationally resolved laser induced fluorescence is described in detail elsewhere [16]. In brief, the laser system consists of a single frequency ring dye laser (Sirah Matisse DS) operated with Rhodamine 6G, pumped with 8 W of the 514 nm line of a  $\text{Ar}^+$ -ion laser (Coherent, Sabre 15 DBW). The dye laser output was coupled into an external folded ring cavity (Spectra Physics Wavetrain) for second harmonic generation. The resulting output power was constant at about 30 mW during the experiment. The molecular beam was formed by co-expanding 5CI, heated to 190 °C, and 400 mbar of argon through a 200  $\mu\text{m}$  nozzle into the vacuum chamber. The molecular beam machine consists of three differentially pumped vacuum chambers that are linearly connected by skimmers (1 mm and 3 mm, respectively) in order to reduce the

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Doppler width. The resulting resolution is 18 MHz (FWHM) in this set-up. In the third chamber, 360 mm downstream of the nozzle, the molecular beam crosses the laser beam at a right angle. The imaging optics setup consists of a concave mirror and two plano-convex lenses to focus the resulting fluorescence onto a photomultiplier tube, which is mounted perpendicularly to the plane defined by the laser and molecular beam. The signal output was then discriminated and digitized by a photon counter and transmitted to a PC for data recording and processing. The relative frequency was determined with a *quasi* confocal Fabry–Perot interferometer. The absolute frequency was obtained by comparing the recorded spectrum to the tabulated lines in the iodine absorption spectrum [17].

## 2.2. Computational methods

### 2.2.1. Quantum chemical calculations

Structure optimizations were performed employing Dunning's correlation consistent polarized valence triple zeta (cc-pVTZ) from the TURBOMOLE library [18,19]. The equilibrium geometries of the electronic ground and the lowest excited singlet states were optimized using the approximate coupled cluster singles and doubles model (CC2) employing the resolution-of-the-identity approximation (RI) [20–22] including spin-component scaling (SCS) modifications to CC2 [23]. All CC2 calculations were carried out utilizing the TURBOMOLE package, version 6.1 [24]. Vibrational frequencies and zero-point corrections to the adiabatic excitation energies have been obtained from numerical second derivatives using the NumForce script [24].

An anharmonic analysis of the vibrational spectrum allows for the determination of vibrational averaging effects due to the individual vibrational motion [25]. Such an anharmonic analysis is implemented in the Gaussian program package [26]. The procedure for the calculation of cubic and of some of the quartic force constants utilizes third derivatives of the potential energy with respect to the normal coordinates. They are calculated for the electronic ground state using numerical derivatives of analytical second derivatives of the MP2 energies using the 6-31G(d,p) basis set. We tried to calculate the same quantities for the excited state vibrational levels using CC2 theory. Since for CC2, only numerical second derivatives are available, numerical instabilities in the calculation of the third derivatives were too large to make the method of any use.

### 2.2.2. Fits of the rovibronic spectra using evolutionary algorithms

The optimization algorithm employed in the fit of molecular constants to the rotationally resolved electronic spectra is an evolutionary strategy adapting mutations *via* a covariance matrix adaptation (CMA-ES) mechanism. This algorithm was developed by Ostermeier et al. [27], and Hansen and Ostermeier [28]. It belongs, like other search algorithms that are also used in our group (genetic algorithms (GAs) [29] and evolutionary strategy employing second generation of derandomized evolutionary strategies (ES-DR2) [30]), to the group of global optimizers that were inspired by natural evolution. For a detailed description of this evolutionary strategy we refer to Refs. [9,29].

## 3. Results and discussion

### 3.1. High resolution spectra of several vibronic bands of 5-cyanoindole

Fig. 1 shows the rotationally resolved spectrum of the electronic origin of 5CI at  $33874\text{ cm}^{-1}$ , taken from the publication by Oeltermann et al. [15]. The authors simulated the experimental spectrum with a rigid rotor Hamiltonian and almost pure *a*-type selection

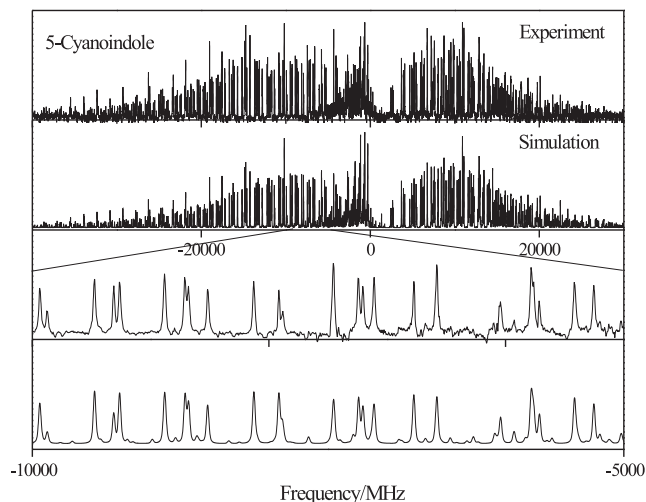


Fig. 1. Rotationally resolved electronic spectrum of the electronic origin of 5-cyanoindole.

rules (the transition dipole moment (TDM) angle  $\theta$  is determined to be  $3^\circ$ , equivalent to less than 1% *b*-type for the spectrum). In the course of the present study we refitted this spectra using the CMA-ES strategy, and the values determined for all molecular parameter are well within the boundaries published previously. To facilitate the comparison for the vibrational bands, these values are given in Table 1. The enlarged portion detail of the spectrum shows the excellent agreement between experiment and simulation using the parameters from the best fit employing the CMA-ES strategy. The fit of the line shapes to Voigt profiles using a Gaussian (Doppler) contribution of  $18\text{ MHz}$  yielded a Lorentzian contribution of  $13 \pm 1\text{ MHz}$  to the total line width equivalent to an excited state life time of  $12 \pm 1\text{ ns}$ , in fair agreement with the value from time-resolved spectroscopy of  $16.9\text{ ns}$  by Huang and Sulkes [14].

The rovibronic spectra of the  $0, 0 + 349$  and  $0, 0 + 884\text{ cm}^{-1}$  bands along with the simulations using the best fit parameters, given in Table 1 are shown in Figs. 2 and 3. In the fit of the molecular parameters to the experimental spectra, we have set the rotational constants of the ground state to the values determined from the fit of the electronic origin. This is justified by the fact, that the signal/noise ratio is nearly two orders of magnitude better for the origin band. Both excited vibronic bands exhibit a considerably larger *b*-type character than the origin band, with TDM angles of  $33^\circ$  and  $23^\circ$ . The lifetime of the  $349\text{ cm}^{-1}$  band increases to  $18 \pm 2\text{ ns}$  compared to  $12 \pm 1\text{ ns}$  for both the origin and the  $884\text{ cm}^{-1}$  band.

## 3.2. Computational results

### 3.2.1. Structure and vibrational averaging

Commonly, the vibrationally averaged inertial parameters, which are obtained from the experiment are compared to equilibrium values at the potential energy minimum, obtained from quantum chemical calculations. Table 1 collects the structural data; i.e., the rotational constants (*A*, *B*, and *C*) in the electronic ground (double prime) and excited (single prime) states, their changes upon electronic excitation ( $\Delta A$ ,  $\Delta B$ , and  $\Delta C$ ), and the respective inertial defects.<sup>1</sup>

<sup>1</sup> The inertial defect is a measure for the non-planarity of a molecule in a given electronic state, and is defined as:  $\Delta I = I_C - I_A - I_B$ . For a planar molecule it is close to zero with out-of-plane vibrations generally causing a negative contribution to the inertial defect, and in-plane vibrations often having a small positive contribution [31].

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