High-resolution laser-induced fluorescence and microwave–ultraviolet double resonance spectroscopy on 1-cyanonaphthalene

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The rotationally resolved fluorescence excitation spectrum of the 0_0^0 band in the $S_1 \leftarrow S_0$ transition of 1-cyanonaphthalene (CNN), at ≈ 318 nm, has been recorded using laser-induced fluorescence in a molecular beam apparatus. This band exhibits pure a-type character and consists of ≈ 600 lines at a rotational temperature of 2.5 K, each with a linewidth of 17 MHz. A microwave–ultraviolet double resonance experiment on the 0_0^0 band of CNN has been performed to verify the rotational assignments of the fluorescence excitation spectrum and to obtain more accurate rotational constants in both the ground and electronically excited states. The band origin of the 0_0^0 band is at 31411.114 ± 0.003 cm^{-1} and the rotational constants are (in MHz) $A'' = 1478.65(2)$, $B'' = 956.75(1)$, $C'' = 580.989(7)$, $A' - A'' = -21.363(9)$, $B' - B'' = -13.305(5)$, and $C' - C'' = -8.167(2)$.

1. Introduction

The combination of supersonic molecular beam expansions and very narrow band lasers is a very powerful tool in experimental molecular spectroscopy. Expanding volatilized organic molecules seeded in a carrier gas gives a cooling of vibrational and rotational degrees of freedom. The advantage for high-resolution spectroscopy is twofold. On the one hand, only the lowest rotational and vibrational levels in the electronic ground state are populated, leading to less dense excitation spectra. On the other hand, owing to the low temperature, stabilization of molecular clusters can occur.

Rotationally resolved laser-induced fluorescence (LIF) spectra can provide detailed information about the geometrical structures in both ground and electronically excited states. Analysis of rotational bands becomes difficult in two cases. First, when the natural lifetime of the excited state is too short, rotational lines become too broad to be resolved resulting in a band contour [1]. Secondly, when the molecule is very large the rotational constants are too small to resolve all the rotational structure in the spectrum. If the molecule under investigation can be described as a rigid symmetric top, the analysis of a partially resolved spectrum is still possible; e.g., triphenylamine and its van der Waals complex with argon [2]. But in the case the molecule has to be described as an asymmetric top, analysis can be difficult due to the large number of unknown molecular parameters; e.g., tetracene–argon complex [3], or due to the presence of hybrid bands [4].

The application of double resonance spectroscopy can be very useful for identifying transitions in spectra of asymmetric rotors [5]. The present paper demonstrates the microwave–ultraviolet double resonance technique for 1-cyanonaphthalene (CNN). This molecule is taken as a test case because it is expected to have a partially resolved spectrum; the rotational constants are expected to be somewhat smaller than those of naphthalene, 1-fluoronaphtha-

lene, 1-hydroxynaphthalene and 1-methylnaphthalene whose spectra have already been measured [6–9], and the natural lifetime of CNN is known to be 22.4 ± 0.2 ns [10], short compared to 1-fluoronaphthalene (110 ns [11]) and 1-methylnaphthalene (353 ns [11]). Therefore, the Lorentzian contribution to the total experimental linewidth in CNN will be 7.1 MHz. The resolution of our UV spectrometer, which consists of a strongly collimated molecular beam and an intracavity frequency-doubled ring dye laser, is 12 MHz [12], so that the experimental linewidth is expected to be on the order of 17 MHz (Voigt profile). Hollas and Thakur [13] showed that several 1-substituted naphthalenes have a transition moment not (totally) parallel to the a inertial axis. Since the CN substituted group exhibits rather similar electronic properties, CNN could be regarded as a possible candidate for a hybrid band.

2. Experimental

An extensive description of the molecular beam apparatus and the narrow band UV laser system has been given elsewhere [6]. Crystalline 1-cyanonaphthalene (Aldrich Chemie, 98%) was heated in a quartz nozzle to approximately 100°C. A molecular beam was formed by a continuous expansion of a mixture of CNN vapor and argon (500–600 Torr) through a nozzle with a diameter of 0.15 mm. The nozzle was kept at a slightly higher temperature to prevent condensation of CNN in the orifice. The molecular beam was skimmed twice in a differential pumping system.

The CNN molecule was resonantly excited from the S_0 to the S_1 state at a distance of 30 cm from the nozzle orifice. The total fluorescence back to the electronic ground state was imaged onto a photomultiplier connected to a photon counting system interfaced with a computer. Narrow band UV radiation was generated by intracavity frequency-doubling a single frequency ring dye laser (a modified Spectra Physics 380D). By using a 2 mm thick $LiIO_3$ crystal, 2 mW of tunable radiation was obtained in the 312–320 nm range with an effective bandwidth of 3 MHz. The excitation spectra of CNN were recorded together with the transmission peaks of a pressure and temperature stabilized interferometer

with a free spectral range of 148 MHz. This value was determined in a microwave–ultraviolet double resonance experiment as will be discussed later. For absolute frequency calibration, the iodine absorption spectrum [14] was recorded.

To perform microwave–ultraviolet (MW–UV) double resonance experiments, microwave radiation was fed into the region where the UV laser interacts with the molecular beam. Microwave radiation with a frequency range between 2 and 10 GHz was generated by a backward wave oscillator (BWO) whose frequency was phase-locked to a harmonic of a synthesizer. The radiation was transported to the vacuum chamber by a coaxial cable and coupled into the excitation region by an antenna mounted on the inner core of the coaxial cable. This antenna was an open loop with a diameter of about 1.5 cm and was positioned in such a way that the laser beam can pass through it. Although this method introduced a lot of stray light, this was the only way to get the MW radiation into the desired region without changing the UV collecting system drastically.

Because of the poor coupling, the intensity of the MW radiation at the crossing point of laser and molecular beam is not known. By amplitude modulation of the MW radiation it is possible to resolve the double resonance signal through digital lock-in techniques. First the UV excitation spectrum is measured. Then the UV frequency is fixed to a (not necessarily totally resolved) rotational transition $(J, K_-, K_+)' \leftarrow (J, K_-, K_+)''$, and the MW frequency is varied until the double resonance signal is found. This MW frequency corresponds to a transition in the vibrationless electronic ground state $(J, K_-, K_+)''_u \leftrightarrow (J, K_-, K_+)''_\ell$ in which $(J, K_-, K_+)''$ is either the upper (subscript u) or lower (ℓ) level. Keeping the MW frequency fixed to this transition and scanning the UV laser while monitoring the double resonance signal gives a spectrum belonging exclusively to electronic transitions originating from $(J, K_-, K_+)''_u$ and $(J, K_-, K_+)3''_\ell$, the last ones with opposite phases. posite phases.

3. Results

In fig. 1 the electronic origin of the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of 1-cyanonaphthalene is
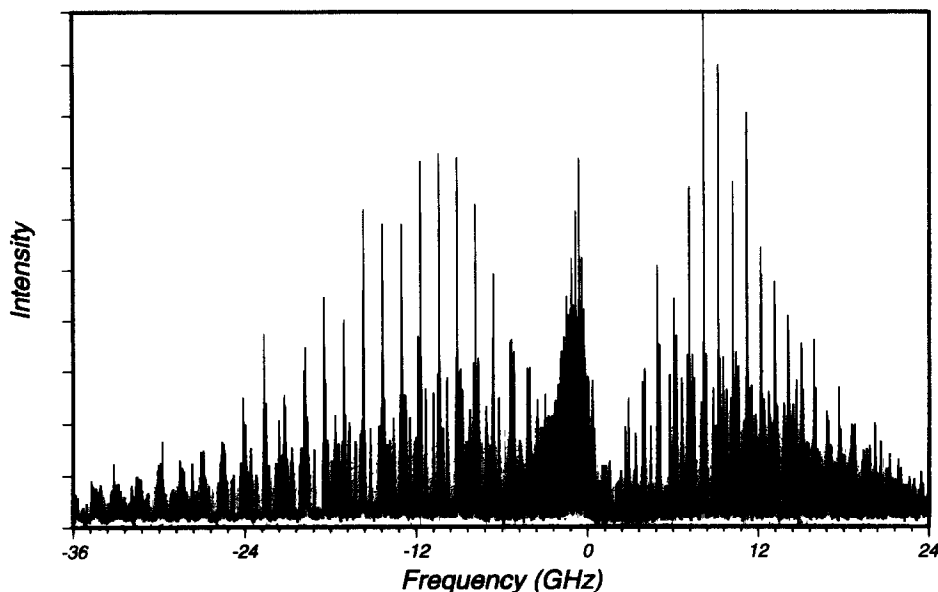
Fig. 1. High-resolution LIF spectrum of the origin of the $S_1 \leftarrow S_0$ transition of 1-cyanonaphthalene. The absolute frequency of the origin (0.0 on the scale of the figure) is at 31411.114 ± 0.003 cm^{-1}.

shown. The absolute frequency of the band origin (0.0 on the scale of the figure) is at 31411.114 ± 0.003 cm^{-1}. The fluorescence is very strong. The signal intensity of the strongest peak is around 700 000 counts/s per mW laser power, whereas there is a continuous background of about 10 000 counts/s per mW due to scattered light. The spectrum contains more than 600 lines and was recorded in less than 10 minutes. In this way the drift of the interferometer during the scan is minimized.

The spectrum shows the characteristic P, Q, and R branch structure and can be identified as an a-type band with selection rules ee$\leftrightarrow$eo and oo$\leftrightarrow$oe for $K'_- K'_+ \leftrightarrow K''_- K''_+$.

As a starting point for the analysis a spectrum was simulated using an asymmetric rotor Hamiltonian and calculated rotational constants obtained from a crude geometrical structure. This spectrum was then compared with the experimental spectrum and an initial assignment was made. The assigned lines were then returned into the fitting program. At the end 170 lines were included in the fit and all parameters were varied simultaneously resulting in a fit with a standard deviation of 4.0 MHz. All lines could be fitted within the experimental accuracy.

Although there is no doubt of the correctness of the assignments a double resonance measurement has been performed for two reasons. In the first place we wanted to investigate this technique for new applications; i.e. to rotationally resolve the electronic excitation spectrum of aromatic molecules in a molecular beam. Secondly, the observation of a number of microwave transitions and fitting simultaneously the microwave and ultraviolet data allows a more accurate determination of the free spectral range of our interferometer that is used for relative frequency calibration of the UV excitation spectra. In addition, more accurate values are obtained for the rotational constants.

Because there were no accurate ground state rotational constants available from other microwave experiments we calculated microwave transitions from the rotational constants resulting from the fit of the $S_1 \leftarrow S_0$ transition, assuming that the dipole moment in the electronic ground state has a component along the a axis. Then, the MW frequency was scanned around the predicted value and continued as has been discussed in the previous section.

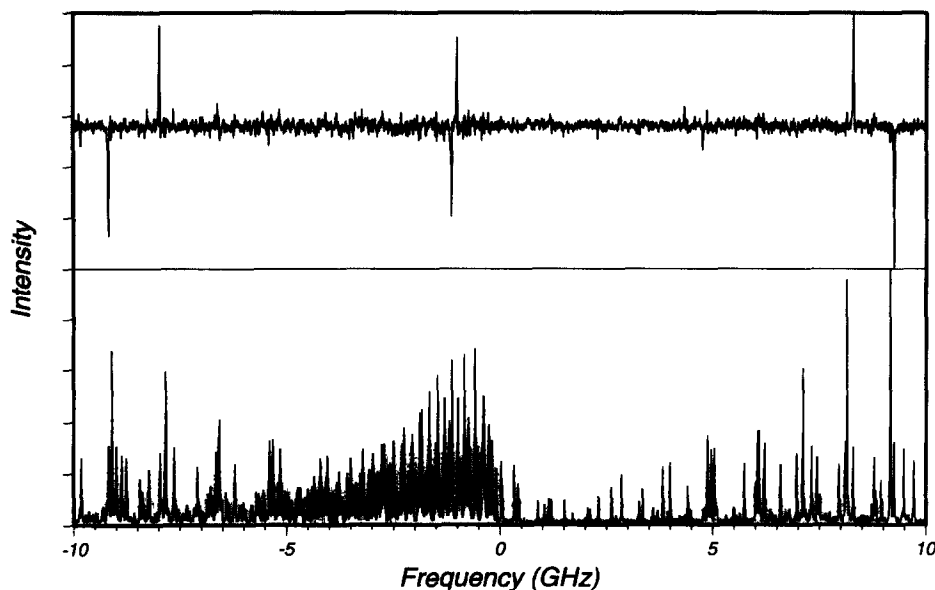Some double resonance spectra are shown in figs. 2 and 3. Individual rotational levels are labeled ac-

Fig. 2. Central part of the microwave–ultraviolet double resonance spectrum of CNN (upper panel). The MW frequency is fixed at 8828 MHz, the UV laser is scanned. The lower panel shows the corresponding part of the UV excitation spectrum. The lines in the double resonance spectrum can be assigned as (from left to right): $(5,1,4)' \leftarrow (6,1,5)''$ and $(4,1,3)' \leftarrow (5,1,4)''$, $(7,7,0)' \leftarrow (7,7,1)''$ and $(7,6,1)' \leftarrow (7,6,2)''$, $(6,1,5)' \leftarrow (5,1,4)''$ and $(7,1,6)' \leftarrow (6,1,5)''$. See text for further details.

cording to the convention $(J, K_-, K_+)''$ and $(J, K_-, K_+)'$ where the double prime denotes the vibrationless electronic ground state and the single prime the electronically excited state.

In the upper panel of fig. 2 the MW frequency has been fixed to the transition $(5,1,4)'' \leftrightarrow (6,1,5)''$ and the UV laser has been scanned over a large frequency interval. One would expect to see two lines with opposite phase in every branch: $(4,1,3)' \leftarrow (5,1,4)''$ and $(5,1,4)' \leftarrow (6,1,5)''$ in the P branch, $(6,1,5)' \leftarrow (5,1,4)''$ and $(7,1,6)' \leftarrow (6,1,5)''$ in the R branch, and $(5,1,5)' \leftarrow (5,1,4)''$ and $(6,1,6)' \leftarrow (6,1,5)''$ in the Q branch. However, a-type electronic transitions in the Q branch involving low K_- values, with respect to J, have very low intensities and are not detectable in our case. Therefore only the two lines on the right and left side of the spectrum can be attributed to a transition involving either $(5,1,4)''$ or $(6,1,5)''$ in the electronic ground state. The origin of the two lines in the center will be discussed later. In the lower panel of fig. 2 part of the UV excitation spectrum in the same frequency range is shown. The reduction of the number of lines in the double resonance spectrum is evident; instead of 600 lines, only

6 lines (in this particular case) are observed.

In fig. 3 an example in the dense part of the Q branch is given. The MW frequency is fixed to a transition with high K_- (with respect to J), $(5,5,0)'' \leftrightarrow (6,5,1)''$. It is clearly seen that the $(5,5,1)' \leftarrow (5,5,0)''$ and $(6,5,2)' \leftarrow (6,5,1)''$ transitions can be resolved from the UV spectrum.

Because the two lines in the middle of the double resonance spectrum of fig. 2 have intensities on the same order of magnitude as lines in the P and R branch, they have to arise from a transition in the Q branch involving high K_- values (with respect to J). Since there are no other a-type microwave transitions (with high K_-) at exactly (i.e. within 1 MHz) the same frequency as the $(5,1,4)'' \leftrightarrow (6,1,5)''$ transition, there could be a microwave b-type transition accidentally at the same frequency. Although one can immediately see that CNN possesses a permanent dipole moment component parallel to the a inertial axis it cannot be ruled out that there exists also a perpendicular component in the plane of the naphthalene molecule, i.e. parallel to the b axis. Indeed the two lines in the center of fig. 2 can be assigned to an a-type UV transition originating from one of the levels
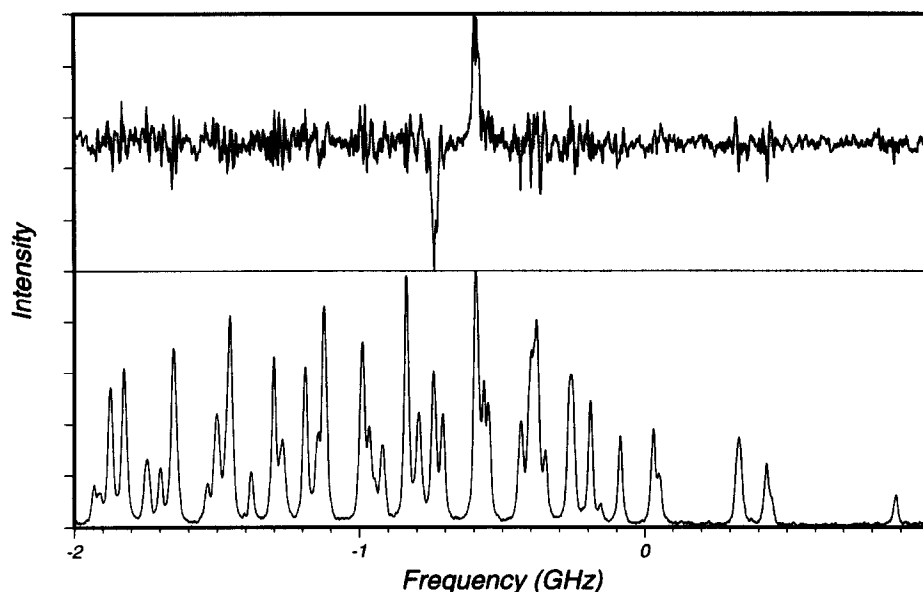
Fig. 3. Part of a MW–UV double resonance spectrum of CNN (upper panel) showing UV transitions in the dense part of the Q branch. The microwave frequency is fixed to the $(5,5,0)'' \leftrightarrow (6,5,1)''$ transition. The lower panel shows the corresponding part of the UV excitation spectrum. The lines in the double resonance spectrum can be assigned as (from left to right): $(6,5,2)' \leftarrow (6,5,1)''$ and $(5,5,1)' \leftarrow (5,5,0)''$.

involved in the b-type microwave transition $(7,6,2)'' \leftrightarrow (7,7,1)''$. For a b-type transition the selection rules are ee$\leftrightarrow$oo and oe$\leftrightarrow$eo for $K'_- K'_+ \leftrightarrow K''_- K''_+$. The UV transitions can thus be assigned as $(7,6,1)' \leftarrow (7,6,2)''$ and $(7,7,0)' \leftarrow (7,7,1)''$. Note that the phases of the lines are correct as compared to those of the P and R lines.

With the double resonance technique we measured 13 microwave transitions (12 a-type, 1 b-type) with an accuracy of about 1 MHz. This last value depends on the lineshape and linewidth of the microwave transition. These 13 transitions and 170 UV transitions have been included in a fitting program in which an extra parameter (a correction factor for the free spectral range of the interferometer) was varied simultaneously, resulting in a fit with a standard deviation of 1.5 MHz. It should be noted that including only 1 b-type MW transition increases the accuracy of the A rotational constant by a factor of 4.

However, the overall precision of the UV data is limited by thermal drift of the frequency markers during the scan of the laser. The magnitude of this error can be determined by scanning the spectrum

several times on various days. From the fit, we obtain the origin of the transition and the rotational constants A, B, and C in the ground state as well as in the excited state. The constants are listed in table 1 together with the asymmetry parameters and the inertial defects.

Table 1
Molecular constants of 1-cyanonaphthalene; the rotational constants A, B, and C (in MHz), the asymmetry parameter κ, and the inertial defect $\Delta I = I_c - I_a - I_b$ (in amu Å^2) in the electronic ground state and their differences with the first excited state ($\Delta A = A' - A''$, etc.)

Molecular constants

A''	1478.65(2)	ΔA	−21.363(9)
B''	956.75(1)	ΔB	−13.305(5)
C''	580.989(7)	ΔC	−8.167(2)
κ''	−0.16280(3)	$\Delta\kappa$	0.0009(1)
$\Delta I''$	−0.15(1)	$\Delta(\Delta I)$	−0.05(2)

band origin 31411.114 ± 0.003 cm^{-1}

With these constants one can calculate the microwave frequencies for the above mentioned a-type $(5,1,4)'' \leftrightarrow (6,1,5)''$ and b-type $(7,6,2)'' \leftrightarrow (7,7,1)''$ transitions. The results are 8828.0 and 8827.4 MHz respectively, both within the experimentally determined linewidth.

The shape of the UV excitation spectrum due to line intensities and linewidths can be simulated by assuming a rotational temperature of 2.5 ± 0.5 K and a linewidth of 17 MHz. The linewidth of our spectrometer is known to be 12 MHz owing to residual Doppler broadening, transit time effects, fluorescence collection optics and laser linewidth, leaving a contribution owing to the lifetime of CNN. This lifetime can be estimated to be about 19 ns, in agreement with the value of 22.4 ± 0.2 ns found by Saigusa et al. [10].

4. Discussion

The rotational constants of 1-cyanonaphthalene have a value of about 75%–80% of those found for other 1-substituted naphthalenes like 1-fluoronaphthalene (FN) [7], 1-methylnaphthalene (MN) [9], 1-hydroxynaphthalene (HN) [8] and 1-aminonaphthalene (AM) [13]. This is not surprising since the attached CN group is heavier than the attached groups in the above mentioned molecules. The inertial defect of the vibrationless electronic ground state of CNN is negative and small, smaller in magnitude than that for naphthalene (-1.4 amu Å^2) [6]. The geometrical structure in this state can thus be described as planar. Exciting CNN to the vibrationless first electronically excited state changes the structure only slightly. The molecule remains planar and, since the rotational constants in the excited state are only a little bit smaller, there is a small increase in the dimensions of the molecule in all directions of the plane.

A more interesting result from our measurements is the direction of the transition moment (TM). Because the experimental spectrum only shows a-type character the TM is parallel to the a inertial axis. This axis makes an angle of 45° with the x axis (i.e. the long axis in naphthalene, see fig. 4). A number of other 1-substituted naphthalenes exhibit hybrid bands. Knowing the intensity ratio of the a- and b-type bands makes it possible to calculate the magni-
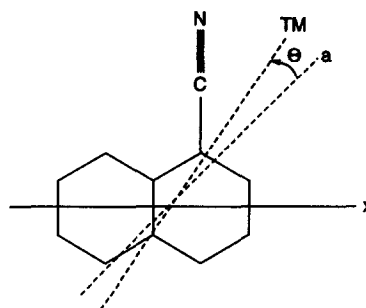

Fig. 4. Schematic of the 1-cyanonaphthalene geometry and the axis system used. The axis labeled with a is the a inertial axis, the one labeled with TM is the transition moment axis. The angles measured in the counterclockwise sense are taken to be positive.

tude (however, not the sign) of the angle θ between the a axis and the TM by using the relation [15]

$$\tan^2\theta = I(b)/I(a) . \tag{1}$$

Both FN and MN have $75\% \pm 5\%$ a-type and $25\% \pm 5\%$ b-type, giving $\theta = \pm 30° \pm 5°$ [7,9]. For HN, two rotamers have been distinguished [8]. The trans-rotamer (t-HN) has $71\% \pm 5\%$ a-type character resulting in $\theta = \pm 33° \pm 5°$, and cis-hydroxynaphthalene (c-HN) is for more than 99% a-type thus having a transition moment parallel to the a axis. A rotational contour analysis performed by Hollas and Thakur [13] of the rather featureless 0_0^0 band of 1-aminonaphthalene (AN) gives a predominant a-type character but the existence of 25% b-type cannot be ruled out. PPP calculations performed by Singh and Thakur [16] show that FN, AN, HN (they did not distinguish the two rotamers) and 1-chloronaphthalene all have the same direction for the transition moment. Their calculation also indicates that one should take the minus sign for θ. Because the a axis makes an angle of 16°–18° with the x axis in the case of FN, HN, AN and MN, the transition moment then will make an angle of $-13°$ to $-16°$ with the x axis (supposing that AN has hybrid character and regarding only t-HN). However, both c-HN and CNN have their transition moment (almost) parallel to the a axis. In this case there is no ambiguity for the direction of the TM. The angles between TM and x axis are 16° and 45°, respectively.

If, however, we take the opposite sign of θ for FN, t-HN, AN and MN the transition moment of all these molecules make an angle between 47° and 48° with

the *x* axis. Although we are speculating, this choice of θ leads to an interesting point of view; all transition moments of the presently studied 1-substituted naphthalenes have a transition moment pointing in the same direction. The different angle for *c*-HN can be attributed to the influence of the lone pair electrons at the oxygen as has been pointed out by Johnson et al. [8].

In this paper, we have shown that microwave–(narrow band) ultraviolet double resonance spectroscopy can be applied to aromatic molecules in a strongly collimated molecular beam. However, owing to the large number of populated levels, even at very low rotational temperatures, one has to be careful in the assignment because of accidentally coinciding microwave transitions as has been demonstrated for 1-cyanonaphthalene. For this molecule we have deduced the rotational constants and the direction of the electronic transition moment. Since the dipole moment in the electronic ground state possesses components along both the *a* axis and *b* axis, MW–UV double resonance spectroscopy especially improves the accuracy of the rotational *A* constant. Comparison of the direction of the transition moment of 1-cyanonaphthalene with other 1-substituted naphthalenes shows that this molecule is one of the few examples having a transition moment parallel to the *a* inertial axis.

Acknowledgement

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