

Rotationally resolved UV spectroscopy of the 2H-tautomer of benzotriazole in a molecular beam

Giel Berden, Erko Jalviste¹, W. Leo Meerts

Department of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

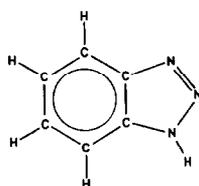
Received 2 June 1994

Abstract

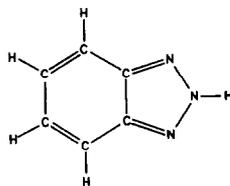
The rotationally resolved excitation spectrum of the 0_0^0 band of the $S_1 \leftarrow S_0$ transition in 2H-benzotriazole, at 286.4 nm, is obtained by using laser-induced fluorescence spectroscopy in a molecular beam. From this pure b-type spectrum, the rotational constants in the ground state and the electronically excited state are determined. The rotational lines are strongly broadened due to the short lifetime which is determined to be around 1.1 ns.

1. Introduction

The tautomerism of benzotriazole has been studied extensively both experimentally and theoretically [1-10]. From quantum chemical calculations [1-3] it is predicted that 1H-benzotriazole (see Fig. 1) is



1H-benzotriazole



2H-benzotriazole

Fig. 1. The two tautomers of benzotriazole. The long in-plane axis is the inertial a axis. The b axis is the short in-plane axis. For 1H-benzotriazole both axes should be rotated counterclockwise around the c axis over an angle of less than 1° (if compared with 2H).

¹ Permanent address: Institute of Physics, Estonian Acad. Sci., Riia 142, Tartu EE2400, Estonia.

more stable than 2H-benzotriazole. Benzotriazole in the solid state exists exclusively as the 1H-tautomer, as has been determined by X-ray crystallography [4]. Also in solution, benzotriazole is predominantly found in the 1H-form as has been shown in a number of studies on benzotriazole and its methyl derivatives by using UV and IR absorption, and NMR techniques (see Refs. [1,2], and references therein).

Only a few gas phase studies have been reported. Maquestiau et al. [5] showed the predominance of the 1H-tautomer in a mass spectrometry experiment, an observation that has been confirmed by photoelectron spectroscopy [6]. Recently, Velino et al. [7] measured the microwave spectrum of benzotriazole and its N-D isotopomer in a heated cell. This spectrum could exclusively be attributed to the 1H-tautomer. The same group reported the rotational band contour of the 0_0^0 band of the $S_1 \leftarrow S_0$ transition of benzotriazole in an absorption measurement [8]. The rotational constants in the excited state were obtained by simulating the band contour keeping the ground rotational constants fixed to the microwave values. They assigned this band to a $\pi^* \leftarrow \pi$ transition

induced in the 1H-tautomer.

Catalan et al. [9] measured the UV absorption spectra of benzotriazole, 1-methylbenzotriazole and 2-methylbenzotriazole in the gas phase in the 220–320 nm range. From a comparison of the three spectra the authors concluded that there is an appreciable amount of 2H-benzotriazole in the vapor. It was also concluded, from measurements at different temperatures (20–80°C), that contrary to ab initio calculations the 2H-tautomer is more stable than 1H-benzotriazole.

All aforementioned gas phase experiments are performed at temperatures higher than room temperature (30–220°C) to ensure a large enough vapor pressure in the gas cell. The first measurements on jet-cooled benzotriazole were performed by Jalviste and Treshchalov [10] by laser-induced fluorescence spectroscopy. They obtained structured vibronic excitation and dispersed fluorescence spectra of the $S_1 \leftarrow S_0$ transition.

In this Letter the rotationally resolved laser-induced fluorescence spectrum of the 0_0^0 band of the $S_1 \leftarrow S_0$ transition of benzotriazole in a supersonic molecular beam is reported. It will be shown that this transition originates from the 2H-tautomer.

2. Experimental

The experimental setup for the high-resolution measurements has been described elsewhere [11]. Only the relevant features are given here. Benzotriazole vapor was obtained by heating crystalline benzotriazole (Janssen Chimica, 98%) in a quartz nozzle to approximately 150°C, and was expanded with argon (backing pressure 0.8 bar) through a nozzle with a diameter of 0.15 mm. The nozzle was kept at a slightly higher temperature to prevent condensation of benzotriazole in the orifice. The molecular beam was skimmed twice in a differential pumping system and was crossed perpendicularly with a UV laser beam at about 30 cm from the beam orifice.

UV radiation with a bandwidth of 3 MHz was generated by intracavity frequency doubling in a single-frequency ring dye laser operating on Rh 110. By using a 2 mm thick Brewster cut BBO crystal, 0.1 mW of tunable radiation was obtained. For relative fre-

quency calibration a temperature stabilized Fabry–Pérot interferometer was used with a free spectral range of 150 MHz. For absolute frequency calibration, the iodine absorption spectrum [12] was recorded simultaneously. The total undispersed fluorescence was imaged on a photomultiplier connected to a photon counting system interfaced with a computer.

3. Results

The absolute frequency of the origin of the $S_1 \leftarrow S_0$ transition of benzotriazole is known within 2 cm^{-1} from the vibrationally resolved LIF spectrum obtained in jet experiments [10]² and from the rotational band contour absorption spectrum obtained in cell experiments [8].

In Figs. 2 and 3, the high-resolution excitation spectrum of this band is shown. The absolute frequency of the band origin (0 on the scale of the figures) is at $34917.759 \pm 0.005 \text{ cm}^{-1}$. The spectrum consists of about 200 not always totally resolved rotational lines. The fluorescence is weak and the rotational lines are strongly broadened due to a short life time. As there is no single isolated Q branch, this band can immediately be identified as predominantly b-type.

As a starting point for the rotational assignment, a b-type spectrum was simulated using a rigid rotor Hamiltonian with rotational constants obtained from microwave measurements [7] and rotational band contour analysis [8]. By comparing the simulation with the experimental spectrum, an initial assignment could be made for the central part of the spectrum, which could then be fitted to give a new set of rotational constants. With this iterative procedure, it was possible to assign all lines in the experimental spectrum. All ground state rotational constants and their differences with the excited state were varied simultaneously resulting in a fit in which all lines could be fitted within their experimental error. The

² The absolute frequencies of the 0_0^0 bands reported in Ref. [10] have been calibrated with neon emission lines. Unfortunately, their wavelengths have not been corrected to vacuum. The corrected frequencies of the origins are 34917 cm^{-1} for benzotriazole and 36022 cm^{-1} for benzimidazole.

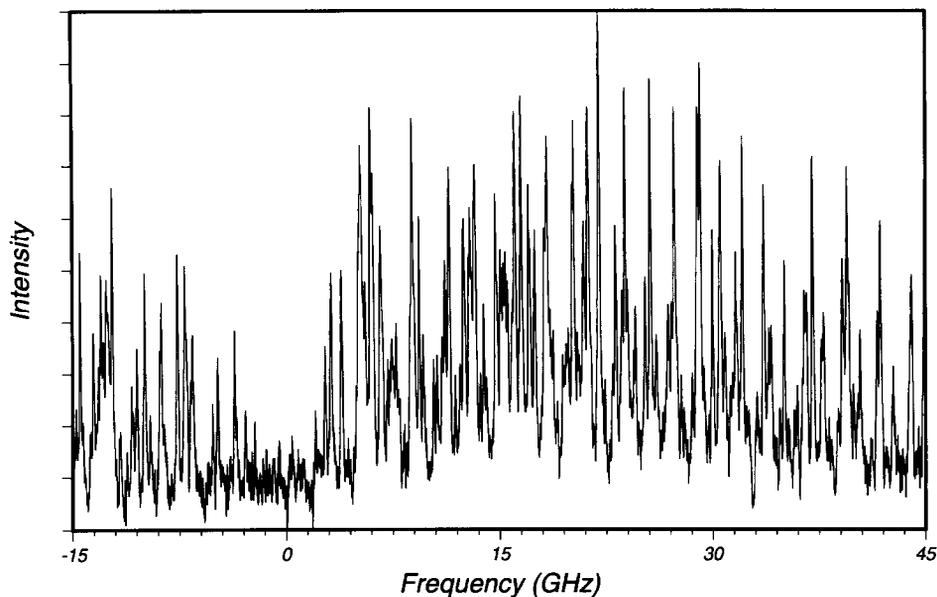


Fig. 2. High-resolution LIF spectrum of the origin of the $S_1 \leftarrow S_0$ transition of 2H-benzotriazole. The absolute frequency of the origin (0 on the scale of the figure) is at $34917.759 \pm 0.005 \text{ cm}^{-1}$.

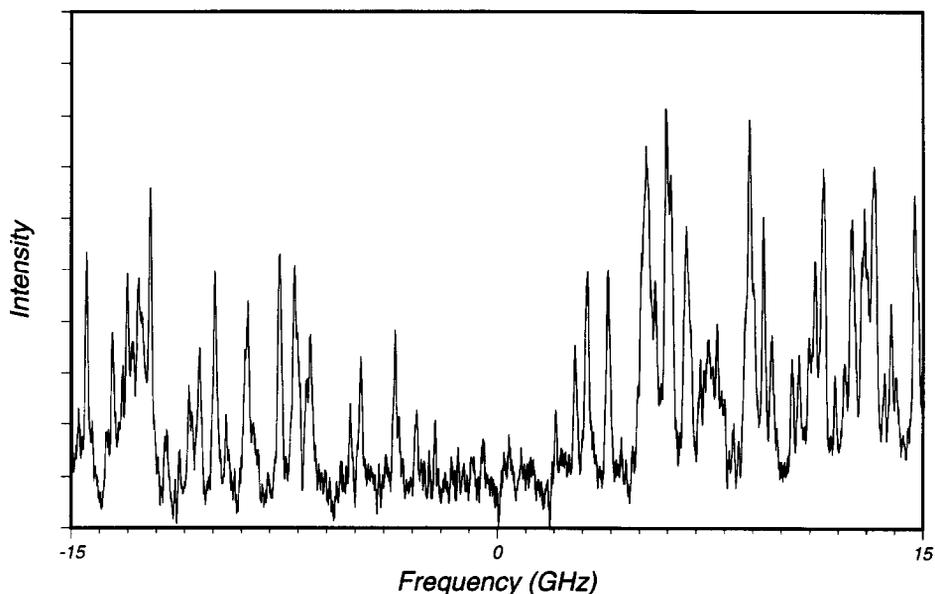


Fig. 3. Central part of the excitation spectrum of 2H-benzotriazole. The laser-induced fluorescence is weak, leading to a signal to noise ratio of only 20. The linewidth of a single rotational line is about 144 MHz as a result of a short lifetime of 1.1 ns.

rotational constants differ considerably from the initial values, and are listed in Table 1, together with the asymmetry parameter and the inertial defect.

There is no indication that the experimental spec-

trum has a hybrid character. This has been confirmed by simulation. The excitation spectrum of the origin of benzotriazole is a pure b-type band. The overall shape of the spectrum could be simulated by

Table 1

Molecular constants of 2H-benzotriazole; 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 $\text{amu } \text{\AA}^2$) in the electronic ground state and their differences with the first excited state ($\Delta A = A' - A''$, etc.)

Molecular constants			
A''	3976(2)	ΔA	-1.2(3)
B''	1699.2(7)	ΔB	-51.86(6)
C''	1190.9(5)	ΔC	-24.92(4)
κ''	-0.6350(8)	$\Delta \kappa$	-0.022(1)
$\Delta I''$	-0.14(20)	$\Delta(\Delta I)$	-0.33(30)
band origin		$34917.759 \pm 0.005 \text{ cm}^{-1}$	

assuming a rotational temperature of about 4 K and a linewidth of 144 ± 9 MHz. Because the experimental linewidth of our spectrometer is known to be about 16 MHz, the largest contribution to the experimental linewidth can be attributed to the short life time which can be determined to be 1.1 ± 0.1 ns.

4. Discussion

Comparing the ground state rotational constants determined from our excitation spectrum with those obtained from microwave spectra [7] shows that there exists a large difference between both sets of constants (see Table 2). Because the microwave data are accurate, we have tried to fit our spectrum keeping the ground state constants fixed to the microwave values. Despite much effort, it was impossible to fit all rotational lines in this way. As has been shown [7], the microwave spectrum belongs to 1H-benzotriazole (the 1-position of the hydrogen has been determined by deuterium substitution), and it is therefore concluded that we have measured the other tautomer, i.e. 2H-benzotriazole.

To ensure that the rotational constants obtained from the spectrum in Fig. 2 belong to the 2H-tautomer, they are compared with calculated values using bond lengths and angles from 6-31G [1,2] and DZ (using a Huzinaga/Dunning double-zeta basis) [3] ab initio calculations, which are listed for both tautomers in Table 2. It can be seen that both DZ and 6-31G methods predict smaller A and larger B and C values for the 2H-tautomer compared to those for the

Table 2

Experimental and calculated values for the ground rotational constants (in MHz) and the permanent dipole moment (in D)

Molecular constants of S_0			
	exp. (UV)	DZ ^a	6-31G ^b
2H-benzotriazole			
A''	3976	4002	4037
B''	1699	1695	1710
C''	1191	1191	1201
μ			0.78
	exp. (MW) ^c	DZ ^a	6-31G ^b
1H-benzotriazole			
A''	4008	4041	4080
B''	1677	1668	1686
C''	1182	1181	1193
μ	4.3	4.64	4.64

^a Calculated from bond lengths and angles taken from Ref. [3].

^b Calculated from bond lengths and angles taken from Refs. [1,2], dipole moment taken from Ref. [1].

^c Obtained from microwave experiments [7].

1H-tautomer in consistence with the experimental data. The DZ calculation predicts the C constant surprisingly precisely. Only slight adjustments of DZ bond lengths ($< 0.005 \text{ \AA}$) and angles ($< 0.01^\circ$), in a way that the structure expands along the b axis and compresses along the a axis, were necessary to reproduce all three experimental constants for the 2H-tautomer.

Comparing the rotational constants in Table 2 shows that the UV transition can be made solely in 2H-benzotriazole, but also in a system in which there is a 2H structure in the ground state and a 1H structure in the excited state. The latter possibility can be rejected because such a large geometry change would lead to an extremely poor Frank-Condon overlap resulting in a practically unobservable spectrum. Since the transition moment lies along the b axis, the observed $S_1 \leftarrow S_0$ transition should be attributed to ${}^1B_2({}^1L_a) \leftarrow {}^1A_1(\pi^* \leftarrow \pi)$ if the following correspondence between inertial and Cartesian axes holds: $a \rightarrow z$, $b \rightarrow y$, $c \rightarrow x$. As can be seen from Table 1, the excited state A constant is almost the same as the ground state one which implies that the molecule is mainly stretched along the a axis upon excitation.

Since the 2H-tautomer has C_{2v} symmetry, there are two pairs of equivalent protons (with nuclear spin

1/2) and one pair of equivalent nitrogen atoms (nuclear spin 1). Analysis of nuclear spin statistics predicts a 78:66 weight ratio for respectively even and odd K_a rotational states. Unfortunately, as a result of laser intensity fluctuations, weak fluorescence, and many overlapping lines (owing to the large line-width) it is impossible to state if there is an intensity alternation as a result of statistical weights.

Obviously now the following question arises: why has the microwave spectrum of 2H-benzotriazole not been observed? First of all, the calculated dipole moment of 2H-benzotriazole (0.78 D) is six times smaller than that of 1H-benzotriazole (4.64 D) [1], giving a 36 times smaller microwave transition probability. Although the experimental value for the 2H-tautomer is not known, it should be noted that the calculated value for 1H-benzotriazole is in good agreement with the experimental value of 4.3 ± 0.4 D [7]. Secondly, the microwave experiment in the gas phase has been performed at high temperature (90°C). Catalán et al. [9] have estimated the proportion of 2H at 80°C to be about 25%. Therefore owing to the smaller dipole moment and the smaller fraction of 2H-benzotriazole at 90°C, the microwave absorption should be roughly 100 times weaker for 2H-benzotriazole than for the 1H-form.

Since it is unlikely that the 0_0^0 bands of the $S_1 \leftarrow S_0$ transitions of 1H-benzotriazole and 2H-benzotriazole are at the same absolute frequency, the electronic absorption spectrum measured in a cell at 140°C and attributed to 1H-benzotriazole in Ref. [7], should be assigned to 2H-benzotriazole. The observation of this band, at this relatively high temperature, supports the results from the UV gas phase study of Catalán et al. [9], who stated that there is still a reasonable amount of 2H-benzotriazole at this temperature. Also the vibrationally resolved jet-cooled spectra reported by Jalviste and Treshchalov [10] have to be attributed to 2H-benzotriazole.

There still remains a problem concerning the $S_1 \leftarrow S_0$ spectrum of 1H-benzotriazole. Both tautomers were shown to contribute to the UV absorption of gas phase benzotriazole in the cell [9], furthermore the sharp

286 nm system (the rotational band contour) was found to be partly superimposed on a strong and diffuse second system [8]. Apart from the possibility that 1H-benzotriazole does not fluoresce, it might also be possible that only the 2H-tautomer is populated under jet conditions as it is more stable [9].

Acknowledgement

EJ gratefully acknowledges the support of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). This work was made possible by financial support from the Dutch Foundation for Fundamental Research on Matter (FOM).

References

- [1] F. Tomás, J.M. Abboud, J. Laynez, R. Notario, L. Santos, S.O. Nilsson, J. Catalán, R.M. Claramunt and J. Elguero, *J. Am. Chem. Soc.* 111 (1989) 7348.
- [2] A.R. Katritzky, K. Yannakopoulou, E. Anders, J. Stevens and M. Szafran, *J. Org. Chem.* 55 (1990) 5683.
- [3] M.H. Palmer, M.M.P. Kurshid, T.J. Rayner and J.A.S. Smith, *Chem. Phys.* 182 (1994) 27.
- [4] A. Escande, J.L. Caligné and J. Lapasset, *J. Acta Cryst. B* 30 (1974) 1490.
- [5] A. Maquestiau, Y. Van Haverbeke, R. Flammang, M.C. Pardo and J. Elguero, *Org. Mass. Spectrom.* 7 (1973) 1267.
- [6] M.H. Palmer and S.M.F. Kennedy, *J. Mol. Struct.* 43 (1978) 203.
- [7] B. Velino, E. Cané, L. Gagliardi, A. Trombetti and W. Caminati, *J. Mol. Spectry.* 161 (1993) 136.
- [8] E. Cané, A. Trombetti and B. Velino, *J. Mol. Spectry.* 158 (1993) 399.
- [9] J. Catalán, P. Pérez and J. Elguero, *J. Org. Chem.* 58 (1993) 5276.
- [10] E. Jalviste and A. Treshchalov, *Chem. Phys.* 172 (1993) 325.
- [11] W.A. Majewski and W.L. Meerts, *J. Mol. Spectry.* 104 (1984) 271.
- [12] S. Gerstenkorn and P. Luc, *Atlas du spectroscopie d'absorption de la molécule d'iode* (CNRS, Paris, 1978); *Rev. Phys. Appl.* 14 (1979) 791.