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SPECTROSCOPIC STUDY OF JET-COOLED BENZOTRIAZOLE

(Presented by K. K. Rebane)

$S_1 \leftarrow S_0$ laser-induced fluorescence excitation spectrum (0–0 band at 34 929 cm⁻¹) and dispersed fluorescence spectra following the excitation into strong vibronic lines of benzotriazole, cooled in a supersonic jet, have been obtained. The rotational contours of different vibronic bands differ substantially. The crude structure of the dispersed fluorescence spectra is determined by a long progression (up to $v=6$) of 1410 cm⁻¹ vibration in S_0 state (asymmetric stretching of the triazole part). It is supposed that different tautomers of benzotriazole correspond to S_0 and S_1 states.

1. Introduction

The use of supersonic molecular beams in preparing cold isolated gas-phase samples for spectroscopic study is a well-known technique nowadays. To our knowledge, from class of benzoderivates of five-membered heterocycles (BDFMH) only indole and its derivates have been investigated thoroughly with a jet-cooling method because indole is the chromophore of amino-acid tryptophan. Information about indole, its derivates and their complexes is derived from investigations of excitation- and dispersed fluorescence spectra [1], rotationally resolved band contours [2], torsional structure in the spectra of methyl-substituted indoles [3] and time-resolved fluorescence [4]. In addition, several nontraditional methods have been developed: rotational coherence spectroscopy by time-resolved fluorescence detection, which has given precise rotational constants for some tryptophan derivates [5] and two-photon fluorescence excitation by linearly/circularly polarized light, which has enabled, for the first time, to identify the bands belonging to 1L_a state in the excitation spectrum of a jet-cooled indole [6].

UV absorption spectra are analysed for vapours of BDFMH molecules benzo(*b*)furan, indole, thianaphthene, indene [6], benzoxazole, benzimidazole, benzothiazole [7] and 2,1,3-benzothiadiazole [8]. For benzotriazole the identified IR and Raman spectra are available [9]. UV absorption, fluorescence, phosphorescence and polarization spectra of indole, indazole, benzimidazole and benzotriazole solutions have been presented in [10]. The spectroscopic study of jet-cooled benzotriazole, reported here, is aimed at obtaining information about the excited states of this molecule.

In principle, there can exist two planar tautomers (1H and 2H) of benzotriazole (Fig. 1) [11]. Unfortunately, no information about tautomers in the gas phase is available. A crystallographic study of solid benzotriazole [12] has revealed only 1H-tautomer. The problem is analogous in the case of 1,2,3-triazole molecule, where 2H-tautomers are the only species observed in the gas phase, while in solution both tautomers can be found [13].

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The near UV singlet-singlet transitions of BDFMH are $\pi^* \leftarrow \pi$ type transitions to two excited electronic states, 1L_a and 1L_b , allowed with in-plane transition dipole moment. For benzotriazole solution in cyclohexan the absorption band origins for 1L_a , 1L_b and 1B_b states are reported to be, respectively, at 34 200, 38 300 and 48 000 cm⁻¹ [10]. These absorption bands are smooth without clearly visible vibrational structure.

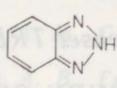
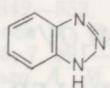


Fig. 1. Tautomers of benzotriazole: 1H-tautomer with C_s symmetry and 2H-tautomer with C_{2v} symmetry.

2. Experimental

Benzotriazole, twice recrystallized from ethanol, was heated in a nozzle chamber to 140 °C and seeded in 0.2 atm Ar gas, then the mixture was expanded into a vacuum through a 0.2 mm orifice. The vacuum of 10⁻³ Torr was maintained with a 700 l/s booster pump NVBM-0.5 backed by a 5 l/s rotary pump 2NVR-5D.

The fluorescence was excited with a frequency-doubled dye laser VL-18 (Rhodamine N and Rhodamine 6G dyes), pumped by ELI-73 excimer laser (typical repetition rate 5Hz). A frequency-doubled unfocused dye laser beam (FWHM 0.4 cm⁻¹, pulse energy 25 μ J, pulse to pulse stability 25%) crossed the jet at 5 mm downstream. The fluorescence excitation spectrum was obtained by measuring the total emission (with f/1 collection optics), the dispersed fluorescence spectra were measured with one half of a DFS-24 0.82 m double monochromator in the second grating order (with f/3.6 condensor). In both cases the signal was detected with a UV photomultiplier FEU-106, processed by a boxcar-integrator BCI-280 and recorded with a chart-recorder.

Although the resolution of VL-18 with an intracavity etalon was 0.1 cm⁻¹ (in UV), the poor pulse-to-pulse stability limited the effective resolution of rotational band contours to 0.3 cm⁻¹. The dye laser and the monochromator were calibrated by using optogalvanic lines of iron/neon hollow cathode lamp. The amount of the scattered light was about 5% of the fluorescence intensity at excitation frequency when the strong bands were excited, therefore no scattering cut-off filter was used.

3. Results and discussion

Fig. 2 shows the $S_1 \leftarrow S_0$ fluorescence excitation spectrum (ES) of jet-cooled benzotriazole. The bands of the spectrum are tabulated in Table 1. The strongest 34929 cm⁻¹ band in ES is assigned to an $S_1 \leftarrow S_0$ origin (0—0 band). For comparision, dispersed fluorescence (DF) spectrum of 0—0 band is presented in Fig. 3. The band frequencies of the spectrum relative to the laser frequency, the combination band assignments and the corresponding IR and Raman frequencies, with mode descriptions taken from [9], are summarized in Table 2.

All bands at the red side from 0—0 band are attributed to hot bands (started from some vibrationally excited ground state level), because their intensity relative to 0—0 band decreases when Ar pressure is raised. The increase of the relative intensity of hot bands is especially pronounced in the excitation spectrum of the stagnation temperature vapour obtained by attenuating the evacuation rate (ambient pressure 0.1 Torr).

The 34 365, 34 390, 34 808, 34 838, 34 929, and 35 409 cm^{-1} bands have hot satellites shifted to the red by about 90 cm^{-1} . If these satellites are caused by 90 cm^{-1} ground-state vibration, then corresponding band must appear in DF spectra. However, in the DF spectrum (Fig. 3) there is no band red-shifted by 90 cm^{-1} from the laser frequency — therefore, the six bands mentioned do not have the same excited state as their satellites have.

The 34 929 ($0-0$), 35 367 and 35 409 cm^{-1} bands have about 560 cm^{-1} red-shifted repetitions: 34 365, 34 808 and 34 847 cm^{-1} hot bands, respectively. This indicates that these hot bands start from 560 cm^{-1} vibrational level of S_0 state. Similar mode frequency appears in the Raman (570 cm^{-1}) and IR (562 cm^{-1}) spectra [9]. However, in the DF spectrum of $0-0$ band there appears only one transition to 538 cm^{-1} ground state vibration, although in ES there exist two strong hot bands (34 365 and 34 390 cm^{-1}) whose distances from $0-0$ band are 564 and 539 cm^{-1} .

The rapid intensity decrease in the ES above $36\,100 \text{ cm}^{-1}$ ($1\,170 \text{ nm}$ from the $0-0$ band), where only weak $36\,210 \text{ cm}^{-1}$ band appears, can be attributed to the increase of the share of nonradiative processes: crossing to a dissociative state, like in the case of indole derivates [4] or an inter-system crossing to some triplet states or an internal conversion into S_0 state. In addition, we can speculate that similar to photoizomerization of

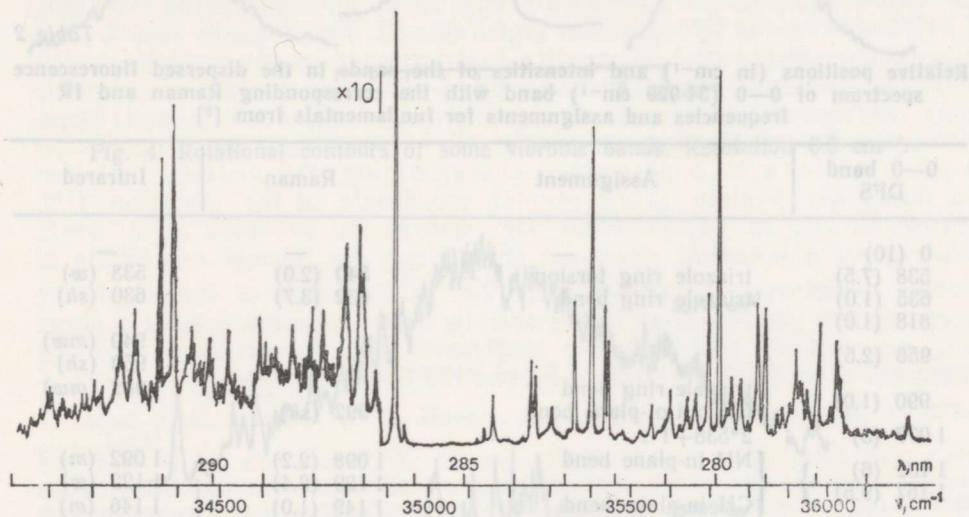


Fig. 2. Fluorescence excitation spectrum of jet-cooled benzotriazole. Band intensities are not normalized to the laser intensity.

Table 1
Vibronic band frequencies (cm^{-1}) and intensities in the fluorescence excitation spectrum.
Absolute accuracy $\pm 2 \text{ cm}^{-1}$

34 272 (<i>vw</i>)	34 847 (<i>w</i>)	35 438 (<i>s</i>)	35 783 (<i>m</i>)
34 302 (<i>vw</i>)	34 929 (<i>vs</i>)	35 448 (<i>s</i>)	35 822 (<i>s</i>)
34 365 (<i>w</i>)	35 167 (<i>w</i>)	35 603 (<i>w</i>)	35 844 (<i>s</i>)
34 390 (<i>w</i>)	35 257 (<i>m</i>)	35 648 (<i>w</i>)	35 911 (<i>m</i>)
34 721 (<i>vw</i>)	35 266 (<i>m</i>)	35 672 (<i>w</i>)	35 970 (<i>s</i>)
34 749 (<i>vw</i>)	35 315 (<i>w</i>)	35 701 (<i>s</i>)	36 024 (<i>m</i>)
34 808 (<i>w</i>)	33 367 (<i>s</i>)	35 724 (<i>vs</i>)	36 210 (<i>w</i>)
34 838 (<i>w</i>)	35 409 (<i>vs</i>)	35 759 (<i>m</i>)	

styrene [14], if the excited state vibrational energy is comparable to the height of the potential barrier between the minima corresponding to the two tautomers (Fig. 1), a tautomerization occurs in S_1 state, which includes new channels for nonradiative processes.

It still remains unclear, if the observed S_1 state is to be assigned to 1L_a or 1L_b .

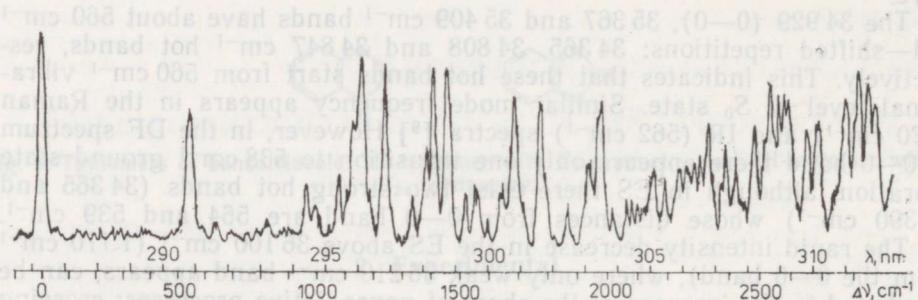


Fig. 3. Dispersed fluorescence spectrum following the excitation into 0-0 band at $34\,929\text{ cm}^{-1}$. Resolution 0.23 nm (26 cm^{-1}).

Table 2

Relative positions (in cm^{-1}) and intensities of the bands in the dispersed fluorescence spectrum of 0-0 ($34\,929\text{ cm}^{-1}$) band with the corresponding Raman and IR frequencies and assignments for fundamentals from [9]

0-0 band DFS	Assignment	Raman	Infrared
0 (10)	—	—	—
538 (7.5)	triazole ring torsion	540 (2.0)	533 (w)
635 (1.0)	triazole ring bend	632 (3.7)	630 (sh)
818 (1.0)			
956 (2.5)	{		940 (mw)
990 (1.0)	{ triazole ring bend		950 (sh)
	CH out-of-plane bend	992 (sh)	982 (mw)
1 077 (3)	2*538+1		
1 132 (6)	{ NH in-plane bend	1 098 (2.2)	1 092 (m)
1 157 (9.5)	{ CH in-plane bend	1 129 (2.4)	1 122 (w)
1 234 (9)	{ triazole ring breath (v_s NNN)	1 149 (1.0)	1 146 (m)
1 335 (2.5)	{ CH in-plane bend	1 211 (2.7)	1 210 (vs)
1 382 (4.5)	{ benzene ring stretch	1 373 (5.3)	1 383 (m)
	triazole ring stretch	1 387 (9.3)	1 420 (m)
1 410 (9)	triazole ring stretch (v_a NNN)		1 458 (m)
1 453 (9)	benzene ring stretch	1 458 (0.6)	
1 517 (2.5)	538+956+23		
1 552 (3)	538+990+24		
1 630 (4)	538+1 077+15		
1 685 (7)	538+1 132+15		
1 702 (4)	538+1 157+7	2 480 (5.5)	1 410+1 077-7
1 776 (7)	538+1 234+4	2 533 (8)	1 410+1 132-9
1 870 (2)	538+1 335-3	2 560 (8)	1 410+1 157-7
1 939 (4.5)	{ 538+1 382+19	2 590 (7)	1 410+1 157+23
	{ 538+1 410-9	2 645 (5.5)	1 410+1 234+1
1 975 (7.5)	538+1 453+16	2 689 (7.5)	1 410+1 237+42
2 153 (3.5)		2 770 (7)	{ 1 410+1 335+25
2 332 (5.5)			{ 1 410+1 382-22
2 388 (5)	1 410+956+22	2 813 (8)	2X1 410-7
2 421 (4)	1 410+990+21	2 856 (9.5)	1 410+1 453-7

The rotational contours of some prominent bands in ES are shown in Fig. 4. The contours of 34929 (0-0) , 35438 cm^{-1} bands and 34365 , 34390 cm^{-1} hot bands are quite similar, but the contours of other bands differ drastically. Such difference is caused by the dependence of rotational constants (molecule geometry) or the direction of the transition

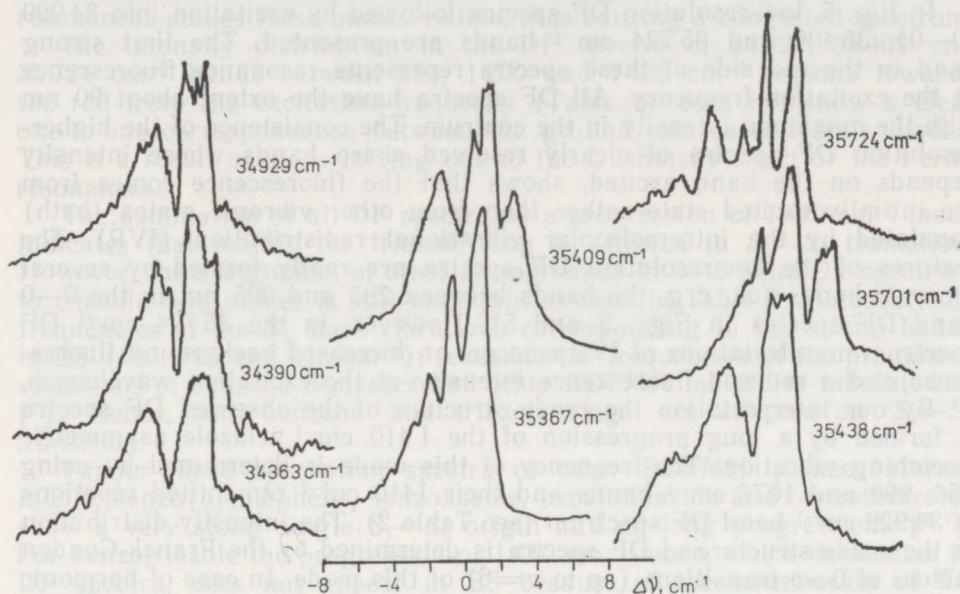


Fig. 4. Rotational contours of some vibronic bands. Resolution 0.3 cm^{-1} .

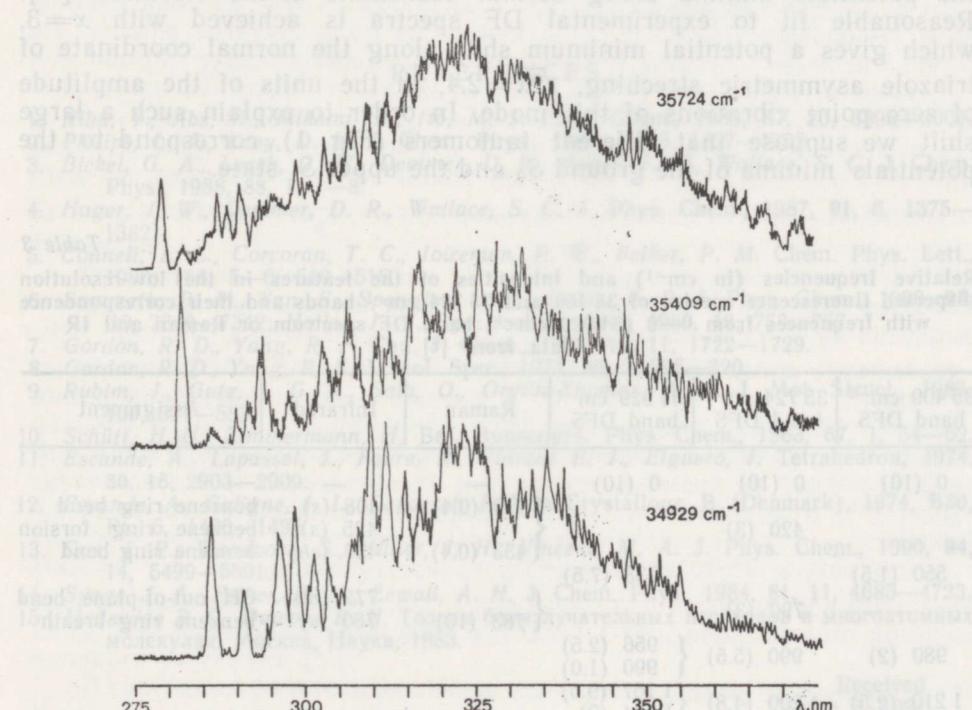


Fig. 5. Dispersed fluorescence spectra from the excitation of 34929 (0-0) , 35409 and 35724 cm^{-1} bands. Resolution 1 nm (115 cm^{-1}).

dipole moment on the vibronic band excited. Both effects can be explained with Hertzberg-Teller vibronic coupling to some upper state(s) allowed by transition(s) with different dipole moment direction. However, the geometrical configuration can be affected also by a strongly unharmonic vibration. The unharmonic potential may be connected with tautomerization in S_1 state.

In Fig. 5, low-resolution DF spectra followed by excitation into $34\ 929$ ($0-0$), $35\ 409$ and $35\ 724\ \text{cm}^{-1}$ bands are presented. The first strong band in the red side of these spectra represents resonance fluorescence at the excitation frequency. All DF spectra have the extent about $90\ \text{nm}$ with the maximum intensity in the centrum. The consistence of the higher-resolution DF spectra of clearly resolved sharp bands whose intensity depends on the band excited, shows that the fluorescence comes from the initially excited state rather than from other vibronic states (bath) populated by the intramolecular vibrational redistribution (IVR). The features of the low-resolution DF spectra are really formed by several vibronic bands (cf., e.g. the bands between 295 and $305\ \text{nm}$ in the $0-0$ band DF spectra in Figs. 3 and 5). However, in the $35\ 724\ \text{cm}^{-1}$ DF spectrum manifestations of IVR emerge: an increased background fluorescence and a reduced fluorescence intensity at the excitation wavelength.

By our interpretation the crude structure of the observed DF spectra is formed by a long progression of the $1\ 410\ \text{cm}^{-1}$ triazole asymmetric stretching vibration. The frequency of this mode is determined by using 956 , 990 and $1077\ \text{cm}^{-1}$ bands and their $1410\ \text{cm}^{-1}$ red-shifted repetitions in $34\ 929\ \text{cm}^{-1}$ band DF spectrum (see Table 2). The intensity distribution in the crude structure of DF spectra is determined by the Franck-Condon factors of $0 \rightarrow v$ transitions (up to $v=6$) of this mode. In case of harmonic upper and ground state potentials with nearly equal vibrational frequencies the Franck-Condon factors for $0 \rightarrow v$ transitions are proportional to $x^v/v!$, where x is a parameter characterizing the distance between the potentials minima along normal coordinate of the vibration [15]. Reasonable fit to experimental DF spectra is achieved with $x=3$, which gives a potential minimum shift along the normal coordinate of triazole asymmetric stretching, $\sqrt{2x}=2.4$, in the units of the amplitude of zero point vibrations of this mode. In order to explain such a large shift we suppose that different tautomers (Fig. 1) correspond to the potentials' minima of the ground S_0 and the upper S_1 state.

Table 3

Relative frequencies (in cm^{-1}) and intensities of the features in the low-resolution dispersed fluorescence spectra of $35\ 409$ and $35\ 724\ \text{cm}^{-1}$ bands and their correspondence with frequencies from $0-0$ ($34\ 929\ \text{cm}^{-1}$) band DF spectrum or Raman and IR data from [9]

$35\ 409\ \text{cm}^{-1}$ band DFS	$35\ 724\ \text{cm}^{-1}$ band DFS	$34\ 929\ \text{cm}^{-1}$ band DFS	Raman	Infrared	Assignment
0 (10)	0 (10)	0 (10)			
	420 (3)		{ 410 (0.4) 433 (0.4)	408 (s) 425 (s) 430 (sh)	benzene ring bend benzene ring torsion benzene ring bend
550 (1.5)		538 (7.5)			
	790 (3)		{ 783 (10)	772 (ms) 780 (s)	CH out-of-plane bend benzene ring breath
980 (2)	990 (5.5)	{ 956 (2.5) 990 (1.0)			
1 210 (2.5)	1 200 (4.8)	{ 1 157 (9.5) 1 234 (9)			
1 420 (6.5)	1 420 (5.5)	{ 1 410 (9) 1 453 (9)			

The congestion of the bands, increasing to the red from the excitation frequency in DF spectra is explained by the increase of the density of S_0 vibrational states with the growth of the vibrational energy. More Fermi-resonances occur between the Franck-Condon allowed vibrations and «dark» combination modes if the density of these modes increases. The intensity redistribution to the combination modes due to the Fermi-resonances makes these modes visible, thus causing a congested spectrum.

The intensity distribution in the DF spectra of 34 929, 35 409 and 35 724 cm^{-1} bands between 990, 1 200 and 1 420 cm^{-1} regions towards the red from the excitation frequency (Table 3) does not show a clear one-to-one correspondence between the ground and excited state modes. This is a result of mode mixing due to the Dushinsky effect or the Fermi resonances.

The domination of all DF spectra by a progression of 1 410 cm^{-1} mode indicates that mainly the triazole ring is affected in $S_1 \leftarrow S_0$ transition. However, the assignment of other strong bands in 0—0 band DF spectrum to triazole ring modes is still uncertain as seen in Table 2. Moreover, the frequencies of the S_1 state vibrations corresponding to the strong bands in ES (480, 795 and 915 cm^{-1}), resemble the frequencies of the prominent vibrations of benzene derivates and other BDFMH molecules tabulated in [7]. Hence, both benzene and triazole rings are affected on $S_1 \leftarrow S_0$ transition.

Vapour-phase absorption spectra of other BDFMH (benzo(*b*)furan, indole, benzo(*b*)thiophene, benzoxazole, benzimidazole and benzothiazole) show a very strong single $S_1 \leftarrow S_0$ origin and no long progressions [6, 7]. For benzotriazole the progression of 1 410 cm^{-1} mode, which dominates in DF spectra, does not appear in ES because of the termination of ES above 1 170 cm^{-1} from $S_1 \leftarrow S_0$ origin due to nonradiative processes.

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JOAS JAHUTATUD BENSOTRIASOOLI SPEKTROSKOOPILINE UURIMINE

On registreeritud ülehelikiirusega joas jahutatud bensotriasooli molekulide laserindutseeritud fluoresentsi $S_1 \leftarrow S_0$ ülemineku ergastusspekter (0—0-joon sagudel $34\,929\text{ cm}^{-1}$) ja tugevate vibroonsete joonte ergastamisel saadud fluorescentsispektrid. Erinevate vibroonjoonte põõlemiskontuuride kuju erineb oluliselt. Fluorescentsispektrite jämeda struktuuri määrab S_0 oleku 1410 cm^{-1} võnkumise (triasooli osa asümmeetrilise venituse) pikki progressioon (kuni $v=6$). Oletatakse, et S_0 - ja S_1 -olekutele vastavad bensotriasooli eri tautomeerid.

Эрко ЯЛВИСТЕ, Алексей ТРЕЩАЛОВ

СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ ОХЛАЖДЕННОГО В СТРУЕ БЕНЗОТРИАЗОЛА

Измерены спектр возбуждения лазерно-индукцированной флуоресценции $S_1 \leftarrow S_0$ -перехода (0—0-линия на частоте $34\,929\text{ cm}^{-1}$) и спектр флуоресценции при возбуждении в интенсивные вибронные линии охлажденных в сверхзвуковой струе молекул бензотриазола. Форма вращательных контуров разных вибронных линий существенно различается. Грубую структуру спектров флуоресценции определяет длинная прогрессия (до $v=6$) колебания 1410 cm^{-1} в S_0 (асимметричное растяжение триазольной части). Предполагается, что S_0 - и S_1 -состояниям соответствуют разные тautомеры бензотриазола.

The spectrum of excitation of laser-induced fluorescence $S_1 \leftarrow S_0$ (0—0-line at frequency $34\,929\text{ cm}^{-1}$) and the spectrum of fluorescence upon excitation in the intense vibrational lines of cooled molecules in the supersonic jet of benzotriazole. The shape of the rotational contours of different vibrational lines is significantly different. The gross structure of the fluorescence spectra is determined by the long progression (up to $v=6$) of the 1410 cm^{-1} vibration in S_0 (asymmetric stretching of the triazolyl part). It is assumed that S_0 - and S_1 -states correspond to different tautomers of benzotriazole.

4	Wavenum 1	A. W. Gerasimov, D. M. Molotov, Z. C. Z. Bulya, C. G. Kozhevnikov, I. V. Klyushnikov, I. A. Trestsalov, 1982, 6, 1828
5	Wavenum 2	I. A. Trestsalov, 1982, 6, 1830
6	Wavenum 3	I. A. Trestsalov, 1982, 6, 1832
7	Wavenum 4	I. A. Trestsalov, 1982, 6, 1834
8	Wavenum 5	I. A. Trestsalov, 1982, 6, 1836
9	Wavenum 6	I. A. Trestsalov, 1982, 6, 1838
10	Wavenum 7	I. A. Trestsalov, 1982, 6, 1840
11	Wavenum 8	I. A. Trestsalov, 1982, 6, 1842
12	Wavenum 9	I. A. Trestsalov, 1982, 6, 1844
13	Wavenum 10	I. A. Trestsalov, 1982, 6, 1846
14	Wavenum 11	I. A. Trestsalov, 1982, 6, 1848
15	Wavenum 12	I. A. Trestsalov, 1982, 6, 1850
16	Wavenum 13	I. A. Trestsalov, 1982, 6, 1852
17	Wavenum 14	I. A. Trestsalov, 1982, 6, 1854
18	Wavenum 15	I. A. Trestsalov, 1982, 6, 1856
19	Wavenum 16	I. A. Trestsalov, 1982, 6, 1858
20	Wavenum 17	I. A. Trestsalov, 1982, 6, 1860
21	Wavenum 18	I. A. Trestsalov, 1982, 6, 1862
22	Wavenum 19	I. A. Trestsalov, 1982, 6, 1864
23	Wavenum 20	I. A. Trestsalov, 1982, 6, 1866
24	Wavenum 21	I. A. Trestsalov, 1982, 6, 1868
25	Wavenum 22	I. A. Trestsalov, 1982, 6, 1870
26	Wavenum 23	I. A. Trestsalov, 1982, 6, 1872
27	Wavenum 24	I. A. Trestsalov, 1982, 6, 1874
28	Wavenum 25	I. A. Trestsalov, 1982, 6, 1876
29	Wavenum 26	I. A. Trestsalov, 1982, 6, 1878
30	Wavenum 27	I. A. Trestsalov, 1982, 6, 1880
31	Wavenum 28	I. A. Trestsalov, 1982, 6, 1882
32	Wavenum 29	I. A. Trestsalov, 1982, 6, 1884
33	Wavenum 30	I. A. Trestsalov, 1982, 6, 1886
34	Wavenum 31	I. A. Trestsalov, 1982, 6, 1888
35	Wavenum 32	I. A. Trestsalov, 1982, 6, 1890
36	Wavenum 33	I. A. Trestsalov, 1982, 6, 1892
37	Wavenum 34	I. A. Trestsalov, 1982, 6, 1894
38	Wavenum 35	I. A. Trestsalov, 1982, 6, 1896
39	Wavenum 36	I. A. Trestsalov, 1982, 6, 1898
40	Wavenum 37	I. A. Trestsalov, 1982, 6, 1900
41	Wavenum 38	I. A. Trestsalov, 1982, 6, 1902
42	Wavenum 39	I. A. Trestsalov, 1982, 6, 1904
43	Wavenum 40	I. A. Trestsalov, 1982, 6, 1906
44	Wavenum 41	I. A. Trestsalov, 1982, 6, 1908
45	Wavenum 42	I. A. Trestsalov, 1982, 6, 1910
46	Wavenum 43	I. A. Trestsalov, 1982, 6, 1912
47	Wavenum 44	I. A. Trestsalov, 1982, 6, 1914
48	Wavenum 45	I. A. Trestsalov, 1982, 6, 1916
49	Wavenum 46	I. A. Trestsalov, 1982, 6, 1918
50	Wavenum 47	I. A. Trestsalov, 1982, 6, 1920
51	Wavenum 48	I. A. Trestsalov, 1982, 6, 1922
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53	Wavenum 50	I. A. Trestsalov, 1982, 6, 1926
54	Wavenum 51	I. A. Trestsalov, 1982, 6, 1928
55	Wavenum 52	I. A. Trestsalov, 1982, 6, 1930
56	Wavenum 53	I. A. Trestsalov, 1982, 6, 1932
57	Wavenum 54	I. A. Trestsalov, 1982, 6, 1934
58	Wavenum 55	I. A. Trestsalov, 1982, 6, 1936
59	Wavenum 56	I. A. Trestsalov, 1982, 6, 1938
60	Wavenum 57	I. A. Trestsalov, 1982, 6, 1940
61	Wavenum 58	I. A. Trestsalov, 1982, 6, 1942
62	Wavenum 59	I. A. Trestsalov, 1982, 6, 1944
63	Wavenum 60	I. A. Trestsalov, 1982, 6, 1946
64	Wavenum 61	I. A. Trestsalov, 1982, 6, 1948
65	Wavenum 62	I. A. Trestsalov, 1982, 6, 1950
66	Wavenum 63	I. A. Trestsalov, 1982, 6, 1952
67	Wavenum 64	I. A. Trestsalov, 1982, 6, 1954
68	Wavenum 65	I. A. Trestsalov, 1982, 6, 1956
69	Wavenum 66	I. A. Trestsalov, 1982, 6, 1958
70	Wavenum 67	I. A. Trestsalov, 1982, 6, 1960
71	Wavenum 68	I. A. Trestsalov, 1982, 6, 1962
72	Wavenum 69	I. A. Trestsalov, 1982, 6, 1964
73	Wavenum 70	I. A. Trestsalov, 1982, 6, 1966
74	Wavenum 71	I. A. Trestsalov, 1982, 6, 1968
75	Wavenum 72	I. A. Trestsalov, 1982, 6, 1970
76	Wavenum 73	I. A. Trestsalov, 1982, 6, 1972
77	Wavenum 74	I. A. Trestsalov, 1982, 6, 1974
78	Wavenum 75	I. A. Trestsalov, 1982, 6, 1976
79	Wavenum 76	I. A. Trestsalov, 1982, 6, 1978
80	Wavenum 77	I. A. Trestsalov, 1982, 6, 1980
81	Wavenum 78	I. A. Trestsalov, 1982, 6, 1982
82	Wavenum 79	I. A. Trestsalov, 1982, 6, 1984
83	Wavenum 80	I. A. Trestsalov, 1982, 6, 1986
84	Wavenum 81	I. A. Trestsalov, 1982, 6, 1988
85	Wavenum 82	I. A. Trestsalov, 1982, 6, 1990
86	Wavenum 83	I. A. Trestsalov, 1982, 6, 1992
87	Wavenum 84	I. A. Trestsalov, 1982, 6, 1994
88	Wavenum 85	I. A. Trestsalov, 1982, 6, 1996
89	Wavenum 86	I. A. Trestsalov, 1982, 6, 1998
90	Wavenum 87	I. A. Trestsalov, 1982, 6, 2000
91	Wavenum 88	I. A. Trestsalov, 1982, 6, 2002
92	Wavenum 89	I. A. Trestsalov, 1982, 6, 2004
93	Wavenum 90	I. A. Trestsalov, 1982, 6, 2006
94	Wavenum 91	I. A. Trestsalov, 1982, 6, 2008
95	Wavenum 92	I. A. Trestsalov, 1982, 6, 2010
96	Wavenum 93	I. A. Trestsalov, 1982, 6, 2012
97	Wavenum 94	I. A. Trestsalov, 1982, 6, 2014
98	Wavenum 95	I. A. Trestsalov, 1982, 6, 2016
99	Wavenum 96	I. A. Trestsalov, 1982, 6, 2018
100	Wavenum 97	I. A. Trestsalov, 1982, 6, 2020
101	Wavenum 98	I. A. Trestsalov, 1982, 6, 2022
102	Wavenum 99	I. A. Trestsalov, 1982, 6, 2024
103	Wavenum 100	I. A. Trestsalov, 1982, 6, 2026
104	Wavenum 101	I. A. Trestsalov, 1982, 6, 2028
105	Wavenum 102	I. A. Trestsalov, 1982, 6, 2030
106	Wavenum 103	I. A. Trestsalov, 1982, 6, 2032
107	Wavenum 104	I. A. Trestsalov, 1982, 6, 2034
108	Wavenum 105	I. A. Trestsalov, 1982, 6, 2036
109	Wavenum 106	I. A. Trestsalov, 1982, 6, 2038
110	Wavenum 107	I. A. Trestsalov, 1982, 6, 2040
111	Wavenum 108	I. A. Trestsalov, 1982, 6, 2042
112	Wavenum 109	I. A. Trestsalov, 1982, 6, 2044
113	Wavenum 110	I. A. Trestsalov, 1982, 6, 2046
114	Wavenum 111	I. A. Trestsalov, 1982, 6, 2048
115	Wavenum 112	I. A. Trestsalov, 1982, 6, 2050
116	Wavenum 113	I. A. Trestsalov, 1982, 6, 2052
117	Wavenum 114	I. A. Trestsalov, 1982, 6, 2054
118	Wavenum 115	I. A. Trestsalov, 1982, 6, 2056
119	Wavenum 116	I. A. Trestsalov, 1982, 6, 2058
120	Wavenum 117	I. A. Trestsalov, 1982, 6, 2060
121	Wavenum 118	I. A. Trestsalov, 1982, 6, 2062
122	Wavenum 119	I. A. Trestsalov, 1982, 6, 2064
123	Wavenum 120	I. A. Trestsalov, 1982, 6, 2066
124	Wavenum 121	I. A. Trestsalov, 1982, 6, 2068
125	Wavenum 122	I. A. Trestsalov, 1982, 6, 2070
126	Wavenum 123	I. A. Trestsalov, 1982, 6, 2072
127	Wavenum 124	I. A. Trestsalov, 1982, 6, 2074
128	Wavenum 125	I. A. Trestsalov, 1982, 6, 2076
129	Wavenum 126	I. A. Trestsalov, 1982, 6, 2078
130	Wavenum 127	I. A. Trestsalov, 1982, 6, 2080
131	Wavenum 128	I. A. Trestsalov, 1982, 6, 2082
132	Wavenum 129	I. A. Trestsalov, 1982, 6, 2084
133	Wavenum 130	I. A. Trestsalov, 1982, 6, 2086
134	Wavenum 131	I. A. Trestsalov, 1982, 6, 2088
135	Wavenum 132	I. A. Trestsalov, 1982, 6, 2090
136	Wavenum 133	I. A. Trestsalov, 1982, 6, 2092
137	Wavenum 134	I. A. Trestsalov, 1982, 6, 2094
138	Wavenum 135	I. A. Trestsalov, 1982, 6, 2096
139	Wavenum 136	I. A. Trestsalov, 1982, 6, 2098
140	Wavenum 137	I. A. Trestsalov, 1982, 6, 2100
141	Wavenum 138	I. A. Trestsalov, 1982, 6, 2102
142	Wavenum 139	I. A. Trestsalov, 1982, 6, 2104
143	Wavenum 140	I. A. Trestsalov, 1982, 6, 2106
144	Wavenum 141	I. A. Trestsalov, 1982, 6, 2108
145	Wavenum 142	I. A. Trestsalov, 1982, 6, 2110
146	Wavenum 143	I. A. Trestsalov, 1982, 6, 2112
147	Wavenum 144	I. A. Trestsalov, 1982, 6, 2114
148	Wavenum 145	I. A. Trestsalov, 1982, 6, 2116
149	Wavenum 146	I. A. Trestsalov, 1982, 6, 2118
150	Wavenum 147	I. A. Trestsalov, 1982, 6, 2120
151	Wavenum 148	I. A. Trestsalov, 1982, 6, 2122
152	Wavenum 149	I. A. Trestsalov, 1982, 6, 2124
153	Wavenum 150	I. A. Trestsalov, 1982, 6, 2126
154	Wavenum 151	I. A. Trestsalov, 1982, 6, 2128
155	Wavenum 152	I. A. Trestsalov, 1982, 6, 2130
156	Wavenum 153	I. A. Trestsalov, 1982, 6, 2132
157	Wavenum 154	I. A. Trestsalov, 1982, 6, 2134
158	Wavenum 155	I. A. Trestsalov, 1982, 6, 2136
159	Wavenum 156	I. A. Trestsalov, 1982, 6, 2138
160	Wavenum 157	I. A. Trestsalov, 1982, 6, 2140
161	Wavenum 158	I. A. Trestsalov, 1982, 6, 2142
162	Wavenum 159	I. A. Trestsalov, 1982, 6, 2144
163	Wavenum 160	I. A. Trestsalov, 1982, 6, 2146
164	Wavenum 161	I. A. Trestsalov, 1982, 6, 2148
165	Wavenum 162	I. A. Trestsalov, 1982, 6, 2150
166	Wavenum 163	I. A. Trestsalov, 1982, 6, 2152
167	Wavenum 164	I. A. Trestsalov, 1982, 6, 2154
168	Wavenum 165	I. A. Trestsalov, 1982, 6, 2156
169	Wavenum 166	I. A. Trestsalov, 1982, 6, 2158
170	Wavenum 167	I. A. Trestsalov, 1982, 6, 2160
171	Wavenum 168	I. A. Trestsalov, 1982, 6, 2162
172	Wavenum 169	I. A. Trestsalov, 1982, 6, 2164
173	Wavenum 170	I. A. Trestsalov, 1982, 6, 2166
174	Wavenum 171	I. A. Trestsalov, 1982, 6, 2168
175	Wavenum 172	I. A. Trestsalov, 1982, 6, 2170
176	Wavenum 173	I. A. Trestsalov, 1982, 6, 2172
177	Wavenum 174	I. A. Trestsalov, 1982, 6, 2174
178	Wavenum 175	I. A. Trestsalov, 1982, 6, 2176
179	Wavenum 176	I. A. Trestsalov, 1982, 6, 2178
180	Wavenum 177	I. A. Trestsalov, 1982, 6, 2180
181	Wavenum 178	I. A. Trestsalov, 1982, 6, 2182
182	Wavenum 179	I. A. Trestsalov, 1982, 6, 2184
183	Wavenum 180	I. A. Trestsalov, 1982, 6, 2186
184	Wavenum 181	I. A. Trestsalov, 1982, 6, 2188
185	Wavenum 182	I. A. Trestsalov, 1982, 6, 2190
186	Wavenum 183	I. A. Trestsalov, 1982, 6, 2192
187	Wavenum 184	I. A. Trestsalov, 1982, 6, 2194
188	Wavenum 185	I. A. Trestsalov, 1982, 6, 2196
189	Wavenum 186	I. A. Trestsalov, 1982, 6, 2198
190	Wavenum 187	I. A. Trestsalov, 1982, 6, 2200
191	Wavenum 188	I. A. Trestsalov, 1982, 6, 2202
192	Wavenum 189	I. A. Trestsalov, 1982, 6, 2204
193	Wavenum 190	I. A. Trestsalov, 1982, 6, 2206
194	Wavenum 191	I. A. Trestsalov, 1982, 6, 2208
195	Wavenum 192	I. A. Trestsalov, 1982, 6, 2210
196	Wavenum 193	I. A. Trestsalov, 1982, 6, 2212
197	Wavenum 194	I. A. Trestsalov, 1982, 6, 2214
198	Wavenum 195	I. A. Trestsalov, 1982, 6, 2216
199	Wavenum 196	I. A. Trestsalov, 1982, 6, 2218
200	Wavenum 197	I. A. Trestsalov, 1982, 6, 2220
201	Wavenum 198	I. A. Trestsalov, 1982, 6, 2222
202	Wavenum 199	I. A. Trestsalov, 1982, 6, 2224
203	Wavenum 200	I. A. Trestsalov, 1982, 6, 2226
204	Wavenum 201	I. A. Trestsalov, 1982, 6, 2228
205	Wavenum 202	I. A. Trestsalov, 1982, 6, 2230
206	Wavenum 203	I. A. Trestsalov, 1982, 6, 2232
207	Wavenum 204	I. A. Trestsalov, 1982, 6, 2234
208	Wavenum 205	I. A. Trestsalov, 1982, 6, 2236
209	Wavenum 206	I. A. Trestsalov, 1982, 6, 2238
210	Wavenum 207	I. A. Trestsalov, 1982, 6, 2240
211	Wavenum 208	I. A. Trestsalov, 1982, 6, 2242
212	Wavenum 209	I. A. Trestsalov, 1982, 6, 2244
213	Wavenum 210	I. A. Trestsalov, 1982, 6, 2246
214	Wavenum 211	I. A. Trestsalov, 1982, 6, 2248
215	Wavenum 212	I. A. Trestsalov, 1982, 6, 2250
216	Wavenum 213	I. A. Trestsalov, 1982, 6, 2252
217	Wavenum 214	I. A. Trestsalov, 1982, 6, 2254
218	Wavenum 215	I. A. Trestsalov, 1982, 6, 2256
219	Wavenum 216	I. A. Trestsalov, 1982, 6, 2258
220	Wavenum 217	I. A. Trestsalov, 1982, 6, 2260
221	Wavenum 218	I. A. Trestsalov, 1982, 6, 2262
222	Wavenum 219	I. A. Trestsalov,