Analysis of Higher Electronic States of Azulene and Its Halogenoderivatives in *n*-Pentane and *n*-Hexane Matrices at 77 K from Absorption Spectra *

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Highly resolved vibrational structures of the $S_2 \leftarrow S_0$ electronic transition and the 0–0 $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ transitions of azulene, 2-chloro-azulene, 1,3-dichloro-azulene, 1,3-dibromo-azulene and 1,3-diiodo-azulene in *n*-pentane and *n*-hexane at 77 K have been obtained and discussed.

The absorption spectra of azulene in alkane solvents consists of four transitions [1, 2]. Highly resolved quasilinear spectra of azulene at 77 K in the range of the first $S_1 \leftarrow S_0$ and the second $S_2 \leftarrow S_0$ electronic transitions were obtained by Ruziewicz and Olszowski [3, 4].

It is very interesting to examine the influence of halogene in azulene in the 2 and 1,3 positions on its spectral properties. In this paper are summarized the results of investigations of higher electronic states ($S_2 \leftarrow S_0$, $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$) of azulene and its halogenoderivatives (e.g. 2-chloro-azulene, 1,3-dichloro-azulene, 1,3-dibromo-azulene and 1,3-diiodo-azulene) in *n*-pentane and *n*-hexane matrices at 77 K from absorption spectra. All the examined compounds are of C_{2v} symmetry.

Experimental

With the exception of azulene (from Fluka), the derivates were synthesized by Eber [5] according to known methods. Purification was achieved by chromatography over alumina. The solvents used were of spectral quality. The measuring arrangement has been described in [6]. In the present investigations a difraction grating (1302 slits/mm) with a reverse linear dispersion of 3,6 Å/mm was used.

Results and Discussion

Table 1 gives the results concerning the multiplet structure in the O-O $S_2 \leftarrow S_0$ transition and the wave numbers of the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ transitions. The $S_2 \leftarrow S_0$ transition shows very narrow absorption lines ($\Delta\tilde{\nu}_{1/2} \approx 10\ \text{cm}^{-1}$) which are grouped in multiplets and which repeat in the vibronic transitions (Shpolskii multiplets [7]).

Azulene and 2-chloro-azulene in *n*-pentane show triplet structure (as well as azulene in *n*-hexane), whereas 2-chloro-azulene in *n*-hexane exhibits sextet structure. This difference is probably due to a more suitable position of the molecule in an *n*-hexane matrix. The spectra of disubstituted azulenes show an octet structure for both matrices. Similar effects were observed for halogenoderivated naphthalenes [8].

It seems to us that the hypothesis of multiplet structure indicating the number of possible positions of the absorbing molecule in the matrix, does not hold.

Calculations for naphthalene were taken up in paper [9], where the Shpolskii multiplets were accounted for in terms of the intramolecular nature.

The $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ absorption transitions consist of narrow but still unresolved bands ($\Delta\tilde{\nu}_{1/2} \approx 50\ \text{cm}^{-1}$). The spectra are similar to those obtained in vapour phase.

The energies of the different O-O transitions and their decrease with the substitution of increasingly heavier atoms can be seen from Table 1. These changes are comparable to those obtained at room temperature in alcoholic solutions [5, 10].

From the frequencies of the normal oscillations in the S_2 state given in Table 2 one can note that the matrix affects neither the frequencies nor the relative intensities of the normal oscillations — within the limits of error.

The substitution of a heavier atom — naturally — results in the occurence of several new frequencies and in a simultaneous disappearence of those found in azulene.

Common frequencies occur in the spectra of 1,3-dihalogeno-azulenes, some of them, e.g. 681 and 1377 cm^{-1}, remain practically unchanged, the other lower systematically on increasing the atomic mass.

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Table 1. Wave numbers of the 0–0 transitions and multiplet structure of the $S_0 \rightarrow S_2$ transitions (in cm^{-1}).

Compound	in n-pentane			in n-hexane			Interpretation
	Int.[a]	$\tilde{\nu}$ (cm^{-1}) 0–0	$\Delta\tilde{\nu}$ (cm^{-1}) mult	Int.[a]	$\tilde{\nu}$ (cm^{-1}) 0–0	$\Delta\tilde{\nu}$ (cm^{-1}) mult	
Azulene	vs	28 202	0	ms	28 181	0	
	m	28 264	62	vvw	28 251	70	$S_0 \rightarrow S_2$ triplet
	w	28 357	155	w	28 334	153	
		33 789			33 749		$S_0 \rightarrow S_3$
		35 410			35 248		$S_0 \rightarrow S_4$
2-Chloro-azulene				vw	27 839	0	
	vw	27 867	0	mw	27 874	35	
	vs	27 895	28	vvw	27 893	54	$S_0 \rightarrow S_2$ triplet
				w	27 907	68	
				vs	27 955	116	and sextet
	ms	27 978	111	vw	27 983	144	
		33 014			33 008		$S_0 \rightarrow S_3$
		34 800			34 794		$S_0 \rightarrow S_4$
1,3-Dichloro-azulene	vvw	26 914	0	vvw	26 975	0	
	m	26 941	27	vw	26 994	19	
	vw	26 962	48	w	27 009	24	$S_0 \rightarrow S_2$
	vw	26 981	67	vw	27 031	56	
	vs	27 001	87	ms	27 051	76	octet
	vvw	27 051	137	s	27 073	98	
	m	27 112	198	vvw	27 105	130	
	vw	27 138	224	ms	27 169	194	
		33 239			33 228		$S_0 \rightarrow S_3$
		34 818			34 855		$S_0 \rightarrow S_4$
1,3-Dibromo-azulene	vvw	26 779	0	vvw	26 898	0	
	m	26 813	34	vw	26 921	23	
	vw	26 846	67	w	26 940	42	
	ms	26 865	86	vs	26 957	59	$S_0 \rightarrow S_2$
	vw	26 888	109	w	26 972	74	
	vvw	26 913	134	vvw	26 990	92	octet
	vvw	26 965	186	vvw	27 052	154	
	mw	26 986	207	ms	27 068	170	
		32 986			32 992		$S_0 \rightarrow S_3$
		34 453			34 447		$S_0 \rightarrow S_4$
1,3-Diiodoazulene				vvw	26 288	0	
				vw	26 304	16	
				w	26 320	32	
				ms	26 338	50	$S_0 \rightarrow S_2$
				vw	26 356	68	
				vvw	26 370	82	octet
				vvw	26 426	138	
				w	26 450	162	
					31 545		$S_0 \rightarrow S_3$
					32 992		$S_0 \rightarrow S_4$

[a] vvs very very strong; vs very strong; s strong; ms middle strong; m middle; mw middle weak; w weak; vw very weak; vvw very very weak.

Such a behaviour of some normal oscillations can be accounted for by the fact that the substitution of various atoms at various sites in azulenes activates other skeleton oscillations. New frequencies occur corresponding to the oscillations of the C-Cl, C-Br and C-I bonds.

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Table 2. Frequencies of normal oscillations of azulene and some halogenoderivatives in S_2 state (in cm^{-1})[a].

Azulene		2-Chloroazulene		1,3-Dichloroazulene		1,3-Dibromoazulene		1,3-Diiodoazulene
in pentane	in hexane	in pentane	in hexane	in pentane	in hexane	in pentane	in hexane	in hexane
							vvw 245	vw 194
		vw 324	w 324					
				mw 427	m 427	w 408	w 409	w 408
vw 672	vvw 675	vw 714	w 715	m 676	s 681	w 682	w 678	m 675
		vw 801	vw 797					
		ms 890	vw 890					vvw 890
m 928	vvw 924	vw 925	m 922					
vs 970	s 963	mw 974	vw 973					
		m 1008	s 1007					
vw 1132		w 1139	m 1125	mw 1103	ms 1084	vw 1075	w 1072	vw 1061
			vw 1155					
s 1309	vw 1298	vvw 1299	vw 1299	ms 1298	mw 1289	w 1277	m 1273	w 1254
				s 1385	ms 1377	vw 1383	mw 1379	mw 1366
			vw 1422					
vvw 1484		vvw 1484	vvw 1482	vw 1479	w 1478	vw 1483	w 1481	vw 1458

[a] Normal frequencies for the most intensive multiplet component are given and intensities are obtained visually.

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