

COMPUTERIZED ASSIGNMENT OF THE BINARY COMBINATION/OVERTONE VIBRATIONAL FREQUENCIES TO INFRARED BANDS OF MONOHALOGENO BENZENES

M. HORÁK^a and A. VÍTEK^b

^a *J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2*

^b *Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6*

Received February 21st, 1973

A program for digital computer was written carrying out an automatic analysis of the binary combination/overtone frequencies in a series of compounds of very similar structure. The complete set of the vibrational fundamental frequencies for each member of the series is needed as input data. The analysis is based on the characteristicity of the vibrational anharmonicities, resonancies are not, however, respected. The program was tested on the series of C_6H_5X ($X = F, Cl, Br, I$) and out of 850 spectral bands in the $4000-150\text{ cm}^{-1}$ region about 85% were interpreted, 15% remaining unassigned by this procedure.

Generally, it is difficult to interpret unambiguously all the bands in the vibrational spectra of molecules with more than ten atoms and in such cases the attention is, first of all, focused to the proper assignment of the fundamental frequencies. With the remaining spectral bands which represent overtones and combinations of the fundamentals the main difficulty stems from the multiplicity of interpretations. In the past, the lack of criteria had prevented elimination or at least reduction of this multiplicity.

In the earlier work¹, the attempt has been made to assign the binary combination/overtone frequencies in 2-halogeno thiophenes (Cl, Br, I). The vibrational spectra of the three compounds are very close together in the whole measured region. To reduce multiplicity of interpretations, the following requirement was introduced: any interpretation must hold for all the three compounds simultaneously. The similarity of the three vibrational spectra is a consequence of characteristicities of normal vibrations of these molecules. In this work, an analysis of binary combination/overtone frequencies was based on the assumption that vibrational anharmonicities of these molecules are also characteristic².

The analysis of the spectra of the halogeno thiophenes¹ has been based on the set of the fundamental frequencies arranged so that they corresponded to the same vibrational modes of the molecules studied. From the set of binary combinations of the fundamentals only those ones complying with the experimental values for all

the three thiophenes have been selected. This restriction greatly reduced the number of individual possibilities.

In principle, such a simultaneous analysis is feasible on digital computers. To verify this idea, a program for Elliott 503 computer was written in Elliott-ALGOL Mk1. language; this program was successfully tested again on the frequencies of 2-halogeno thiophenes, the analysis of which was described earlier¹. It was employed in analyzing the frequencies of 4-halogeno derivatives of diphenyl ether³, and in this work for the assignment of the combination/overtone vibrational frequencies of monohalogeno benzenes.

Similar attempt for the computerised analysis of the overtone/composition frequencies was made by Pince and Poilblanc⁴, but these authors analysed only one compound at one time and made no attempts to solve the multiplicity of the assignment.

Description of the Algorithm

For each compound studied, the two column vectors are stored in the computer memory: the vector of all the experimental frequencies, v_k , $k \in \langle 1, m \rangle$, arranged in the decreasing order and the column vector of the n fundamental frequencies, v_i^{fund} , $i \in \langle 1, n \rangle$. The latter forms a matrix in such a manner that the elements corresponding to the same vibrational mode in the series are on one row. Furthermore, several intervals of possible values of anharmonicities $\langle A_{\min}, A_{\max} \rangle$ are chosen for the given series of compounds and a maximal allowable dispersion of anharmonicities $D_{\max}(A)$ is estimated.

The algorithm consists of the following steps:

1. For a given combination of indices i and j ($i \leq j \leq n$), the sum $v_i^{\text{fund}} + v_j^{\text{fund}} = v$ is evaluated for each compound. The experimental frequency v_k fulfilling the condition $\text{Min}_{k \in \langle 1, m \rangle} |v - v_k|$ is found and the anharmonicity $A = v - v_k$ is computed.

2. It is tested if the condition $A \in \langle A_{\min}, A_{\max} \rangle$, is met for all the compounds. If not then go back to step 1.

3. The mean value $M(A)$ of anharmonicities computed in step 1 and their dispersions $D(A)$ are evaluated. If $D(A)$ is greater than the limiting value of $D_{\max}(A)$, then go to step 4, else the combination $(v_i^{\text{fund}} + v_j^{\text{fund}})$ is written in the output file together with the additional information including the resulting symmetry class. Now, existence of the difference combination tone $|v_i - v_j|$ is tested in a similar way (steps 2 and 3). The algorithm continues by step 1.

4. The compound with the greatest difference between its anharmonicity A and the mean value $M(A)$ is found. With respect to the sign of the difference $(A - M(A))$, the value of k is changed to $(k + 1)$ or $(k - 1)$. If a new value $k \in \langle 1, m \rangle$, then $A = v - v_k$ is re-evaluated and followed by step 2 else step 1.

After exhausting all the combinations of i and j , the output file is sorted according to a chosen key and it is printed out.

The printed results should be carefully checked because the algorithm does not respect possible resonancies among/between close vibrational levels. Moreover, such a final check verifies the original assignment of the fundamental frequencies which could be in error.

TABLE I

Input Data: Arranged Fundamental Frequencies from Infrared and Raman^a Spectra of Liquid Halogeno Benzenes C₆H₅X (X = F, Cl, Br, I)

i^b	S ^c	Wavenumber, cm ⁻¹				Assignment
		F	Cl	Br	I	
1	A ₁	3 102	3 083	3 078	3 072	CH stretching
2	A ₁	3 086	3 070	3 067	3 066	CH stretching
3	B ₂	3 064	3 060	3 059	3 059	CH stretching
4	A ₁	3 050	3 028	3 027	3 018	CH stretching
5	B ₂	3 038	3 017	3 005	2 996	CH stretching
6	A ₁	1 597	1 586	1 580	1 573	ring stretching
7	B ₂	1 597	1 586	1 580	1 573	ring stretching
8	A ₁	1 497	1 479	1 477	1 473	ring stretching
9	B ₂	1 458	1 447	1 446	1 439	ring stretching
10	B ₂	1 327	1 327	1 323	1 323	ring stretching
11	B ₂	1 285	1 274	1 266	1 263	CH in-plane bending
12	A ₁	1 220	1 084	1 071	1 063	X-sensitive
13	A ₁	1 156	1 173	1 175	1 177	CH in-plane bending
14	B ₂	1 156	1 157	1 160	1 159	CH in-plane bending
15	B ₂	1 067	1 068	1 071	1 060	CH in-plane bending
16	A ₁	1 023	1 024	1 021	1 016	CH in-plane bending
17	A ₁	1 009	1 004	1 002	998	ring stretching
18	B ₁	982	986	988	988	CH out-of-plane bending
19	A ₂	962	966	965	965	CH out-of-plane bending
20	B ₁	898	904	905	904	CH out-of-plane bending
21	A ₂	833	831	832	835	CH out-of-plane bending
22	A ₁	807	703	673	654	X-sensitive
23	B ₁	754	740	736	730	CH out-of-plane bending
24	B ₁	686	685	685	685	ring bending
25	B ₂	614	614	613	612	ring bending
26	A ₁	520	419	314	266 ^a	X-sensitive
27	B ₁	501	470	457	450	X-sensitive
28	A ₂	407	406	404	400	ring bending
29	B ₂	407	297	251 ^a	220 ^a	X-sensitive
30	B ₁	242 ^a	195 ^a	180 ^a	166 ^a	X-sensitive

^a The Raman frequency. ^b Index; the numbering according to Whiffen⁵. ^c Symmetry species.

TABLE II
Output Data: Assignment and Anharmonicity Parameters of the Vibrational Frequencies of Halo-
geno Benzenes C_6H_5X in the $4000 - 150\text{ cm}^{-1}$ Region^a

Indices ^b $i \pm j$	S_r^c	Wavenumbers ν and anharmonicities A , cm^{-1}								$M(A)^d$	$D(A)^e$
		X = F		X = Cl		X = Br		X = I			
		ν	A	ν	A	ν	A	ν	A		
3 20	A_2	3 965	3	3 970	6	3 964	0	3 952	-11	0	42
4 20	B_1	3 942	-6	3 918	-14	3 932	0	3 914	-8	-7	25
5 20	A_2	3 942	6	3 918	-3	3 910	0	3 901	1	1	11
3 21	B_1	3 902	5	3 901	10	3 892	1	3 901	7	6	11
1 22	A_1	3 902	-7	3 786	0	3 752	1	3 728	2	-1	13
4 21	A_2	3 891	8	3 870	11	3 855	-4	3 846	-7	2	59
2 22	A_1	3 891	-2	3 774	1	3 740	0	3 728	8	2	14
1 23	B_1	3 868	12	3 834	11	3 820	6	3 801	-1	7	27
3 22	B_2	3 868	-3	3 764	1	3 726	-6	3 711	-2	-2	7
4 22	A_1	3 868	11	3 743	12	3 709	9	3 685	13	11	2
2 23	B_1	3 838	-2	3 814	4	3 802	-1	3 801	5	2	10
5 22	B_2	3 838	-7	3 701	-19	3 669	-9	3 643	-7	-10	25
2 24	B_1	3 762	-10	3 753	-2	3 752	0	3 749	-2	-3	15
3 24	A_2	3 753	3	3 743	-2	3 740	-4	3 749	5	1	14
5 24	A_2	3 732	8	3 701	-1	3 693	3	3 685	4	4	11
1 25	B_2	3 712	-4	3 701	4	3 693	2	3 685	1	1	9
4 25	B_2	3 662	-2	3 639	-3	3 635	-5	3 626	-4	-3	2
5 25	A_1	3 647	-5	3 615	-16	3 609	-9	3 601	-7	-9	17
1 26	A_1	3 614	-8	3 490	-12	3 379	-13	3 334	-4	-9	13
1 27	B_1	3 603	0	3 549	-4	3 539	4	3 514	-8	-2	20
2 26	A_1	3 603	-3	3 490	1	3 379	-2	3 334	2	0	5
2 27	B_1	3 592	5	3 533	-7	3 517	-7	3 514	-2	-3	24
3 27	A_2	3 568	3	3 533	3	3 517	1	3 514	5	3	2
3 26	B_2	3 568	-16	3 470	-9	3 368	-5	3 316	-9	-10	16
4 26	A_1	3 568	-2	3 448	1	3 335	-6	3 281	-3	-2	7
4 27	B_1	3 554	3	3 490	-8	3 493	9	3 477	9	3	48
5 27	A_2	3 543	4	3 490	3	3 457	-5	3 450	4	2	15
1 28	A_2	3 514	5	3 490	1	3 493	11	3 477	5	6	13
1 29	B_2	3 514	5	3 382	2	3 335	6	3 281	-11	1	47
2 29	B_2	3 493	0	3 368	1	3 313	-5	3 281	-5	-2	8
3 29	A_1	3 478	7	3 368	11	3 313	3	3 281	2	6	13
3 28	B_1	3 455	-16	3 467	1	3 457	-6	3 450	-9	-7	38
2 30	B_1	3 327	-1	3 260	-5	3 239	-8	3 233	1	-3	12
3 30	A_2	3 320	14	3 260	5	3 239	0	3 233	8	7	26
6 7	B_2	3 195	1	3 166	-6	3 160	0	3 145	-1	-1	8
1 -	A_1	3 102		3 083		3 078		3 072			
2 -	A_1	3 086		3 070		3 067		3 066			
3 -	B_2	3 064		3 060		3 059		3 059			

TABLE II
(Continued)

Indices ^b $i \pm j$	S_r^c	Wavenumbers ν and anharmonicities, A , cm^{-1}								$M(A)^d$	$D(A)^e$
		X = F		X = Cl		X = Br		X = I			
		ν	A	ν	A	ν	A	ν	A		
4 —	A_1	3 050		3 028		3 027		3 018			
9 6/7 ^f	B_2/A_1^f	3 050	— 5	3 028	— 5	3 027	1	3 018	6	— 1	21
5 —	B_2	3 038		3 017		3 005		2 996			
8 8	A_1	2 986	— 8	2 952	— 6	2 944	— 10	2 937	— 9	— 8	2
8 9	B_2	2 950	— 5	2 921	— 5	2 915	— 8	2 906	— 6	— 6	2
10 6/7	B_2/A_1	2 912	— 12	2 907	— 6	2 905	2	2 895	— 1	— 4	28
9 9	A_1	2 912	— 4	2 888	— 6	2 883	— 9	2 875	— 3	— 5	6
11 6/7	B_2/A_1	2 876	— 6	2 851	— 9	2 839	— 7	2 834	— 2	— 6	7
3 — 30 ^d	A_2	2 822	0	2 879	14	2 883	4	2 895	2	5	29
8 10	B_2	2 817	— 7	2 798	— 8	2 793	— 7	2 788	— 8	— 7	1
12 6/7	A_1/B_2	2 812	— 5	2 665	— 5	2 646	— 5	2 628	— 8	— 6	2
9 10	A_1	2 780	— 5	2 775	1	2 770	1	2 762	0	— 1	6
13 6/7	A_1/B_2	2 757	4	2 758	— 1	2 760	5	2 753	3	3	5
14 6/7	B_2/A_1	2 748	— 5	2 741	— 2	2 736	— 4	2 729	— 3	— 3	2
9 11	A_1	2 744	1	2 717	— 4	2 706	— 6	2 698	— 4	— 3	7
8 12	A_1	2 712	— 5	2 559	— 4	2 541	— 7	2 536	0	— 4	7
1 — 29	B_2	2 700	5	2 798	12	2 839	12	2 864	12	10	9
3 — 28	B_1	2 657	0	2 650	— 4	2 646	— 9	2 656	— 3	— 4	11
10 10	2 657	2 657	3	2 650	— 4	2 646	0	2 645	— 1	0	7
15 6/7	B_2/A_1	2 657	— 7	2 650	— 4	2 646	— 5	2 628	— 5	— 5	1
8 13	A_1	2 649	— 4	2 650	— 2	2 646	— 6	2 645	— 5	— 4	2
9 13	B_2	2 613	— 1	2 618	— 2	2 616	— 5	2 614	— 2	— 2	3
9 14	A_1	2 613	— 1	2 601	— 3	2 593	— 13	2 594	— 4	— 5	21
10 11	A_1	2 613	1	2 601	0	2 593	4	2 583	— 3	1	7
17 6/7	A_1/B_2	2 613	7	2 584	— 6	2 576	— 6	2 572	1	— 1	30
18 6/7	B_1/A_2	2 578	— 1	2 564	— 8	2 568	0	2 566	5	— 1	22
19 6/7	A_2/B_1	2 563	4	2 546	— 6	2 541	— 4	2 536	— 2	— 2	14
8 15	B_2	2 563	— 1	2 546	— 1	2 541	— 7	2 536	3	— 1	13
11 11	A_1	2 563	— 7	2 546	— 2	2 522	— 10	2 527	1	— 4	19
10 12	B_2	2 546	— 1	2 407	— 4	2 388	— 6	2 378	— 8	— 5	7
9 15	A_1	2 522	— 3	2 513	— 2	2 508	— 9	2 495	— 4	— 4	8
8 16	A_1	2 515	— 5	2 497	— 6	2 495	— 3	2 486	— 3	— 4	2
20 6/7	B_1/A_2	2 504	9	2 497	7	2 495	10	2 486	9	9	1
8 17	A_1	2 504	— 2	2 479	— 4	2 474	— 5	2 470	— 1	— 3	3
11 12	B_2	2 504	— 1	2 364	6	2 333	— 4	2 318	— 8	— 2	26
10 13	B_2	2 485	2	2 497	— 3	2 495	— 3	2 503	3	0	8
10 14	A_1	2 485	2	2 479	— 5	2 474	— 9	2 479	— 3	— 4	16
8 18	B_1	2 485	6	2 473	8	2 474	9	2 466	5	7	3
9 16	B_2	2 485	4	2 473	2	2 474	7	2 454	— 1	3	9

TABLE II
(Continued)

Indices ^b $i \pm j$	S_r^c	Wavenumbers ν and anharmonicities, A , cm^{-1}								$M(A)^d$	$D(A)^e$
		X = F		X = Cl		X = Br		X = I			
		ν	A	ν	A	ν	A	ν	A		
9 17	B_2	2 453	-14	2 448	-3	2 444	-3	2 436	-1	-5	26
11 13	B_2	2 443	2	2 448	1	2 444	3	2 447	7	3	5
12 12	A_1	2 443	3	2 162	-6	2 146	4	2 123	-3	0	18
11 14	A_1	2 433	-8	2 428	-3	2 419	-7	2 417	-5	-6	4
9 19	B_1	2 433	13	2 428	15	2 419	8	2 407	3	10	22
8 20	B_1	2 400	5	2 392	9	2 388	6	2 378	1	5	8
22 6/7	A_1/B_2	2 400	-4	2 284	-5	2 242	-11	2 216	-11	-8	11
12 13	A_1	2 373	-3	2 255	-2	2 242	-4	2 234	-6	-4	2
12 14	B_2	2 373	-3	2 243	2	2 230	-1	2 216	-6	-2	9
4 -24	B_1	2 364	0	2 335	-8	2 349	7	2 334	1	0	29
10 16	B_2	2 349	-1	2 364	13	2 349	5	2 342	3	5	26
11 15	A_1	2 349	-3	2 335	-7	2 333	-4	2 318	-5	-5	2
23 6/7	B_1/A_2	2 349	-2	2 325	-1	2 318	2	2 318	15	4	47
13 13	A_1	2 312	0	2 335	-11	2 349	-1	2 355	1	-3	23
13 14	B_2	2 312	0	2 325	-5	2 333	-2	2 334	-2	-2	3
11 17	B_2	2 300	6	2 284	6	2 270	2	2 273	12	7	13
8 22	A_1	2 300	-4	2 181	-1	2 146	-4	2 123	-4	-3	2
9 21	B_1	2 285	-6	2 274	-4	2 270	-8	2 273	-1	-5	7
12 15	B_2	2 285	-2	2 152	0	2 146	4	2 123	0	1	5
11 18	A_2	2 260	-7	2 255	-5	2 242	-12	2 248	-3	-7	11
8 23	B_1	2 260	9	2 226	7	2 215	2	2 205	2	5	10
9 22	B_2	2 260	-5	2 152	2	2 116	-3	2 094	1	-1	8
13 15	B_2	2 222	-1	2 243	2	2 242	-4	2 234	-3	-1	6
14 15	A_1	2 222	-1	2 226	1	2 230	-1	2 216	-3	-1	2
25 6/7	B_2/A_1	2 204	-7	2 197	-3	2 195	2	2 189	4	-1	19
9 23	A_2	2 204	-8	2 181	-6	2 178	-4	2 163	-6	-6	2
12 18	B_1	2 204	2	2 066	-4	2 056	-3	2 055	4	0	11
13 16	A_1	2 176	-3	2 197	0	2 195	-1	2 189	-4	-2	3
14 16	B_2	2 176	-3	2 181	0	2 178	-3	2 171	-4	-2	3
8 24	B_1	2 176	-7	2 162	-2	2 156	-6	2 153	-5	-5	4
12 19	A_2	2 176	-6	2 048	-2	2 039	3	2 029	1	-1	12
13 17	A_1	2 166	1	2 181	4	2 178	1	2 171	-4	1	9
14 17	B_2	2 166	1	2 162	1	2 156	-6	2 153	-4	-2	10
9 24	A_2	2 154	10	2 135	3	2 136	5	2 123	-1	4	16
13 18	B_1	2 132	-6	2 152	-7	2 156	-7	2 163	-2	-5	5
15 15	A_1	2 132	-2	2 135	-1	2 146	4	2 123	3	1	7
14 18	A_2	2 132	-6	2 135	-8	2 146	-2	2 133	-14	-7	19
10 22	B_2	2 132	-2	2 025	-5	1 999	3	1 977	0	-1	9
13 19	A_2	2 114	-4	2 135	-4	2 136	-4	2 133	-9	-5	5

TABLE II
(Continued)

Indices ^b <i>i</i> ± <i>j</i>	<i>S_r</i> ^c	Wavenumbers ν and anharmonicities, <i>A</i> , cm ⁻¹								<i>M(A)</i> ^d	<i>D(A)</i> ^e	
		X = F		X = Cl		X = Br		X = I				
		ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>			
14	19	B ₁	2 114	- 4	2 125	2	2 116	- 9	2 123	- 1	- 3	17
11	21	B ₁	2 114	- 4	2 098	- 7	2 087	-11	2 094	- 4	- 6	9
12	20	B ₁	2 114	- 4	1 984	- 4	1 980	4	1 963	- 4	- 2	12
8	25	B ₂	2 107	- 4	2 091	- 2	2 087	- 3	2 082	- 3	- 3	1
27	6/7	B _{1/A₂}	2 107	9	2 060	4	2 039	2	2 020	- 3	3	19
15	16	B ₂	2 086	- 4	2 091	- 1	2 087	- 5	2 073	- 3	- 3	2
10	23	A ₂	2 086	5	2 066	- 1	2 056	- 3	2 055	2	1	9
15	17	B ₂	2 072	- 4	2 066	- 6	2 068	- 5	2 055	- 3	- 4	2
9	25	A ₁	2 072	0	2 060	- 1	2 056	- 3	2 055	4	0	7
15	18	A ₂	2 035	-14	2 048	- 6	2 056	- 3	2 038	-10	- 8	17
16	17	A ₁	2 035	3	2 025	- 3	2 020	- 3	2 013	- 1	- 1	6
17	17	A ₁	2 023	5	2 003	- 5	1 999	- 5	1 994	- 2	- 2	17
12	22	A ₁	2 023	- 4	1 789	2	1 742	- 2	1 713	- 4	- 2	6
13	21	A ₂	1 986	- 3	2 003	- 1	1 999	- 8	2 013	1	- 3	11
16	19	A ₂	1 986	1	1 984	- 6	1 980	- 6	1 977	- 4	- 4	8
29	6/7	B _{2/A₂}	1 986	-18	1 882	- 1	1 830	- 1	1 794	1	- 5	59
9	26	B ₂	1 986	8	1 863	- 3	1 757	- 3	1 702	- 3	0	23
12	23	B ₁	1 986	12	1 825	1	1 806	- 1	1 794	1	3	26
18	18	A ₁	1 961	- 3	1 963	- 9	1 980	4	1 977	1	- 2	24
15	20	A ₂	1 961	- 4	1 963	- 9	1 980	4	1 963	- 1	- 2	23
17	19	A ₂	1 961	-10	1 963	- 7	1 962	- 5	1 963	0	- 5	14
14	22	B ₂	1 961	- 2	1 863	3	1 830	- 3	1 812	- 1	- 1	5
18	19	B ₂	1 938	- 6	1 944	- 8	1 943	-10	1 944	- 9	- 8	2
11	25	A ₁	1 903	4	1 882	- 6	1 882	3	1 883	8	2	26
18	20	A ₁	1 874	- 6	1 882	- 8	1 882	-11	1 883	- 9	- 8	4
19	20	B ₂	1 855	- 5	1 863	- 7	1 864	- 6	1 864	- 5	- 6	1
9	29	A ₁	1 855	-10	1 731	-13	1 695	- 2	1 652	- 7	- 8	17
18	21	B ₂	1 828	13	1 825	8	1 830	10	1 825	2	8	16
15	23	A ₂	1 828	7	1 805	- 3	1 806	- 1	1 794	4	2	16
10	27	A ₂	1 828	0	1 789	- 8	1 771	- 9	1 770	- 3	- 5	14
16	22	A ₁	1 828	- 2	1 731	4	1 695	1	1 669	- 1	1	6
12	25	B ₂	1 828	- 6	1 698	0	1 685	1	1 669	- 6	- 3	11
19	21	A ₁	1 796	1	1 789	- 8	1 790	- 7	1 794	- 6	- 5	13
11	26	B ₂	1 796	- 9	1 698	5	1 580	0	1 526	- 3	- 2	26
13	25	B ₂	1 776	6	1 789	2	1 790	2	1 794	5	4	3
18	22	B ₁	1 776	-13	1 686	- 3	1 654	- 7	1 636	- 6	- 7	13
19	22	A ₂	1 776	7	1 670	1	1 639	1	1 628	9	5	13
20	21	B ₂	1 735	4	1 731	- 4	1 732	- 5	1 735	- 4	- 2	13
18	23	A ₁	1 735	- 1	1 731	5	1 732	8	1 713	- 5	2	26

TABLE II
(Continued)

Indices ^b $i \pm j$	S_r^c	Wavenumbers ν and anharmonicities, A , cm^{-1}								$M(A)^d$	$D(A)^e$	
		X = F		X = Cl		X = Br		X = I				
		ν	A	ν	A	ν	A	ν	A			
8	30	B_1	1 735	- 4	1 670	- 4	1 654	- 3	1 636	- 3	- 3	1
10	29	A_1	1 735	1	1 624	0	1 575	1	1 548	5	2	4
12	26	A_1	1 735	- 5	1 496	- 7	1 385	0	1 323	- 6	- 4	8
16	24	B_1	1 715	6	1 706	- 3	1 701	- 5	1 702	1	0	18
19	23	B_2	1 715	- 1	1 706	0	1 701	0	1 696	1	0	1
17	24	B_1	1 695	0	1 686	- 3	1 685	- 2	1 682	- 1	- 1	2
11	28	B_1	1 695	3	1 686	6	1 669	- 1	1 669	6	4	9
11	29	A_1	1 695	3	1 568	- 3	1 514	- 3	1 473	-10	- 3	21
15	25	A_1	1 686	5	1 686	4	1 685	1	1 669	- 3	2	10
21	21	A_1	1 675	9	1 664	2	1 669	5	1 669	- 1	4	14
13	26	A_1	1 675	- 1	1 586	- 6	1 477	-12	1 439	- 4	- 6	16
14	26	B_2	1 675	- 1	1 568	- 8	1 477	3	1 426	1	- 1	17
20	23	A_1	1 654	2	1 646	2	1 639	- 2	1 636	2	1	3
16	25	B_2	1 647	10	1 638	0	1 639	5	1 628	0	4	17
21	22	A_2	1 647	7	1 540	6	1 514	9	1 501	12	9	6
12	28	A_2	1 624	- 3	1 496	6	1 477	2	1 460	- 3	1	15
6/7	—	A_1/B_2	1 597		1 586		1 580		1 573			
20	24	A_1	1 579	- 5	1 586	- 3	1 580	-10	1 587	- 2	- 5	10
15	26	B_2	1 579	- 8	1 479	- 8	1 385	0	1 323	- 3	- 5	12
14	28	B_1	1 561	- 2	1 561	- 2	1 575	11	1 562	3	3	29
14	29	A_1	1 561	- 2	1 457	3	1 413	2	1 381	2	1	4
22	23	B_1	1 561	0	1 447	4	1 413	4	1 381	- 3	1	9
16	26	A_1	1 541	- 2	1 447	4	1 335	0	1 293	11	3	25
21	24	B_2	1 527	8	1 523	7	1 514	- 3	1 521	1	3	20
17	26	A_1	1 527	- 2	1 417	- 6	1 323	7	1 263	- 1	0	23
23	23	A_1	1 510	2	1 479	- 1	1 477	5	1 460	0	2	6
8	—	A_1	1 497		1 479		1 477		1 473			
22	24	B_1	1 497	4	1 389	1	1 361	3	1 350	11	5	14
15	28	B_1	1 480	6	1 479	5	1 477	2	1 460	0	3	6
18	27	A_1	1 480	- 3	1 457	1	1 446	1	1 439	1	0	3
19	26	A_2	1 480	- 2	1 389	4	1 286	7	1 235	4	3	11
15	29	A_1	1 480	6	1 373	8	1 335	13	1 293	13	10	10
9	—	B_2	1 458		1 447		1 446		1 439			
23	24	A_1	1 445	5	1 430	5	1 413	- 8	1 426	11	3	48
16	29	B_2	1 430	0	1 327	6	1 274	2	1 235	- 1	2	7
17	28	A_2	1 413	- 3	1 417	7	1 413	7	1 393	- 5	2	31
17	29	B_2	1 413	- 3	1 300	- 1	1 266	13	1 222	4	3	38
20	27	A_1	1 395	- 4	1 373	- 1	1 361	- 1	1 350	- 4	- 2	3
19	28	A_1	1 375	6	1 373	1	1 385	16	1 373	8	8	29

TABLE II
(Continued)

Indices ^b $i \pm j$		S_r^c	Wavenumbers ν and anharmonicities, A , cm^{-1}								$M(A)^d$	$D(A)^e$
			X = F		X = Cl		X = Br		X = U			
			ν	A	ν	A	ν	A	ν	A		
24	24	A_1	1 375	3	1 373	3	1 361	- 9	1 373	3	0	27
21	26	A_2	1 360	- 3	1 237	-13	1 147	1	1 094	- 7	- 5	27
10	-	B_2	1 327		1 327		1 323		1 323			
22	26	A_1	1 327	0	1 124	2	988	1	922	2	1	1
24	25	A_2	1 303	3	1 300	1	1 302	4	1 302	5	3	2
22	27	B_1	1 303	- 5	1 173	0	1 132	2	1 094	-10	- 3	22
11	-	B_2	1 285		1 274		1 266		1 263			
23	26	B_1	1 285	11	1 157	- 2	1 054	4	998	2	4	22
23	27	A_1	1 253	- 2	1 213	3	1 196	3	1 177	- 3	0	8
25	25	A_1	1 234	6	1 237	9	1 234	8	1 235	11	9	4
21	29	B_1	1 234	- 6	1 124	- 4	1 071	-12	1 051	- 4	- 6	11
22	28	A_2	1 220	6	1 118	9	1 071	- 6	1 051	- 3	2	39
12	-	A_1	1 220		1 084		1 071		1 063			
19	30	B_2	1 200	- 4	1 157	- 4	1 147	2	1 123	- 8	- 3	13
24	27	A_1	1 188	1	1 157	2	1 147	5	1 123	-12	- 1	43
13	-	A_1	1 156		1 173		1 175		1 177			
14	-	B_2	1 156		1 157		1 160		1 159			
6/7	-27	B_1/A_2	1 105	9	1 118	2	1 132	9	1 123	0	5	17
15	-	B_2	1 067		1 068		1 071		1 060			
21	30	B_2	1 067	- 8	1 024	- 2	1 010	- 2	998	- 3	- 4	6
26	26	A_1	1 037	- 3	831	- 7	627	- 1	530	- 2	- 3	5
16	-	A_1	1 023		1 024		1 021		1 016			
25	28	B_1	1 023	2	1 024	4	1 021	4	1 016	4	4	1
17	-	A_1	1 009		1 004		1 002		998			
27	27	A_1	998	- 4	937	- 3	914	0	904	4	- 1	10
18	-	B_1	982		986		988		988			
19	-	A_2	962		966		965		965			
26	29	B_2	925	- 2	703	-13	560	- 5	491	5	- 4	42
27	28	B_2	915	7	867	- 9	862	1	853	3	1	35
20	-	B_1	898		904		905		904			
11	-28	B_1	878	0	867	- 1	862	0	860	- 3	- 1	2
21	-	A_2	833		831		832		835			
28	28	A_1	807	- 7	814	2	805	- 3	793	- 7	- 4	14
22	-	A_1	807		703		673		654			
29	29	A_1	807	- 7	585	- 9	491	-11	433	- 7	- 8	3
14	-29	A_1	754	5	867	7	914	5	940	1	5	5
23	-	B_1	754		740		736		730			
26	30	B_1	754	- 8	614	0	491	- 3	433	1	- 2	13
24	-	B_1	686		685		685		685			

TABLE II
(Continued)

Indices ^b $i \pm j$		S_r^c	Wavenumbers ν and anharmonicities, A , cm^{-1}								$M(A)^d$	$D(A)^e$
			X = F		X = Cl		X = Br		X = I			
			ν	A	ν	A	ν	A	ν	A		
29	30	A_2	652	3	494	2	440	9	398	12	7	18
25	—	B_2	614		614		613		612			
19	—28	A_1	561	6	555	— 5	560	— 1	567	2	1	17
13	—25	B_2	535	— 7	555	— 4	560	— 2	567	2	— 3	11
26	—	A_1	520		419		314		266*			
27	—	B_1	501		470		457		450			
17	—26	A_1	485	— 4	585	0	685	— 3	730	— 2	— 2	2
28	—	A_2	407		406		404		400			
29	—	B_2	407		297		251*		220*			
30	—	B_1	242*		195*		180*		166*			

^a The Raman frequencies⁶ are marked by asterisks. ^b The combination of indices of the fundamental frequencies from Table I; the negative value of j means a difference combination $\nu_i - \nu_j$. ^c The resulting symmetry species $S_r = S_1 \times S_j$. ^d Mean value of anharmonicities A_X , (X = F, Cl, Br, I). ^e Dispersion of anharmonicities A_X , $D(A) = (M(A) - A)^2/4$. ^f The fundamental frequencies Nos 6 and 7 are equal.

Analysis of the Spectra of C_6H_5X (X = F, Cl, Br, I)

To attain the good consistency of data, we re-measured the known IR spectra of liquid halogeno benzenes (of analytical grade purity). The absorption curves were recorded on a Perkin-Elmer grating spectrometer, model 621. The overall accuracy of the readings was about $\pm 2 \text{ cm}^{-1}$ due to low intensities and larger half-band widths of bands corresponding to the overtone/combination frequencies. The table of 30 fundamentals for the molecule C_6H_5X (Table I) was arranged according to Whiffen's assignment⁵, the Raman frequencies were taken from ref.⁶.

The table of all the experimental frequencies contained roughly seven times more data. The results of the computerized analysis after manual check are presented in Table II. The intervals of anharmonicities used covered the range from $\langle -5, +1 \rangle$ to $\langle -20, +50 \rangle$, the value of $D_{\max}(A)$ was chosen to be 50. The time needed for one analysis did not exceed 1 minute (at 100,000 op/s). From about 850 bands in all the spectra, 85% of the bands were interpreted, 15% of them remained unassigned by this procedure.

In our experience, computer programs of this type are useful tools for analysis of the vibrational spectra of larger polyatomic molecules. First of all, validity of the

assignment of the fundamentals is verified and, furthermore, regularities in intensities of overtone/combination bands can be discovered and the rules for them established. Such a computerized analysis economizes treatment of data and gives a more reliable warranty to the results. It is noteworthy, however, that the procedure described is suitable only for cases of molecules with very similar structure, vibrational coupling, anharmonicities, *etc.*

REFERENCES

1. Horák M., Hyams I. J., Lippincott E. R.: *Spectrochim. Acta* 22, 1355 (1966).
2. Papoušek D.: *This Journal* 29, 2277 (1964).
3. Garrigou-Lagrange C., Horák M., Khanna R. K., Lippincott E. R.: *This Journal* 35, 3230 (1970).
4. Pince R., Poilblanc R.: *Spectrochim. Acta* 28A, 907 (1972).
5. Whiffen D. H.: *J. Chem. Soc.* 1956, 1350.
6. Kohlrausch K. W. F., Wittek H.: *Monatsh. Chem.* 74, 1 (1943).

Translated by R. Řeřicha.