The Infra-red Spectra of the Monohalogenonaphthalenes.

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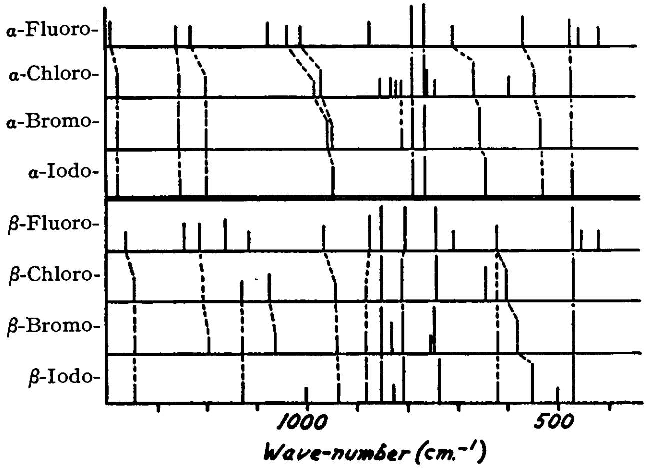
Recent work on the ultra-violet absorption and phosphorescence of monohalogenonaphthalenes has necessitated a knowledge of their vibration frequencies. To this end the infra-red spectra have been examined in *cyclo*hexane and also as pure liquids and solids. Certain relations have been suggested, and two frequencies discussed in relation to ultra-violet absorption.

IN view of work on the absorption spectra (Ferguson, *J.*, 1954, 304) and the phosphorescence (Ferguson, Iredale, and Taylor, *J.*, 1954, 3160) of monohalogenonaphthalenes, it is necessary to obtain information about their vibration frequencies. Raman spectra have been published for α-fluoro- and β-bromo- (Goekel, *Z. physikal. Chem.*, 1935, *B*, **29**, 79; Luther, *Z. Elektrochem.*, 1948, **52**, 210), α- and β-chloro- (Goekel, *loc. cit.*; Luther, *loc. cit.*; Ziemecki, *Z. Physik*, 1932, **78**, 123), and α-bromo-naphthalene (Goekel, *loc. cit.*; Luther, *loc. cit.*; Ziemecki, *loc. cit.*; Dadieu and Kohlrausch, *Monatsh.*, 1931, **57**, 488).



Specific infra-red data for monohalogenonaphthalenes are lacking, although they have been included in a general presentation of the infra-red frequencies of substituted naphthalenes by Lecomte (*Compt. rend.*, 1939, **208**, 1636). In order to fill this deficiency we have examined their spectra in the region 400—1400 cm.$^{-1}$ in *cyclo*hexane solution, the α-series also as pure liquids and the β-series as solids. The frequencies found are contained in Tables 1—4. A detailed discussion of them and of their relation to the naphthalene fundamentals is not possible. We have therefore included a line diagram of the frequencies found, and shown possible relations by means of broken lines. These trends, although tentative, help to show major differences between the α- and the β-series.

A most interesting feature of their spectra is the appearance of the fundamental 470 cm.$^{-1}$ in both series. It is unaltered both by type of substituent and position in the ring. This vibration is the counterpart of the controversial 473 vibration of naphthalene. Its probable appearance in the absorption spectra of these compounds has been discussed (Ferguson, *loc. cit.*).

Luther (*loc. cit.*) has derived an empirical equation for determining the value of the naphthalene 764 a_g fundamental (ω_4 in Luther's notation) in the α-substituted derivatives. We find that this Raman-active vibration is also strongly infra-red active, recording the good coincidences shown in Table 5.

TABLE 1. *Infra-red frequencies of α-halogenonaphthalenes in* cyclo*hexane.*

α-Fluoro-	α-Chloro-	α-Bromo-	α-Iodo-	α-Fluoro-	α-Chloro-	α-Bromo-	α-Iodo-
414 m	—	—	—	—	808 m	807 m	—
456 m	—	—	—		821 m	—	—
473 ms	471 ms	470 m	471 m	—	830 m	—	—
567 s	541 ms	532 ms	525 m	—	852 m	—	—
—	595 m	—	—	874 ms			
709 m	663 ms	650 s	642 s	1011 m	969 ms	948 m	
—	740 m	—	—	1036 m	984 m	956 ms	944 ms
—	758 ms	—	—	1074 ms	—	—	—
764 vs	764 vs	763 vs	762 vs	1229 m	1201 m	1197 m	1199 m
791 vs	789 vs	788 vs	787 vs	1258 m	1252 m	1253 ms	1253 m
				1391 m	1375 m	1376 ms	1380 m

In all Tables, w = weak, mw = medium to weak, m = medium, ms = medium to strong, s = strong, vs = very strong.

TABLE 2. *Infra-red frequencies of* β-*halogenonaphthalenes in* cyclo*hexane.*

β-Fluoro-	β-Chloro-	β-Bromo-	β-Iodo-	β-Fluoro-	β-Chloro-	β-Bromo-	β-Iodo-
418 m	—	—	—	804 vs	808 vs	807 vs	807 vs
454 m	—	—	—	—	—	832 s	824 m
471 s	471 s	470 vs	469 s	851 vs	851 vs	851 vs	851 vs
—	—	—	548 ms	871 ms	879 m	882 m	881 m
—	603 ms	581 s	—	963 m	941 m	939 m	934 m
620 ms	622 m	620 m	617 mw	—	1075 m	1063 m	—
—	641 ms	—	—	1112 m	1128 m	1130 m	1128 m
707 m	—	—	—	1160 ms	—	—	—
738 vs	740 vs	741 vs	737 vs	1214 ms	—	1192 m	—
—	—	757 m	—	1246 ms	—	—	—
				1360 m	1345 m	1344 m	1342 m

TABLE 3. *Infra-red frequencies of* α-*halogenonaphthalenes in the liquid state.*

α-Fluoro-	α-Chloro-	α-Bromo-	α-Iodo-	α-Fluoro-	α-Chloro-	α-Bromo-	α-Iodo-
415 m	—	—	—	1011 m	983 w	956 ms	967 w
455 m	—	—	—	1035 m	—	—	1020 m
473 m	472 m	471 m	472 m	1074 ms	1143 m	—	1128 m
567 s	541 s	532 ms	524 ms	1229 s	1200 ms	1199 m	1199 ms
—	494 m	—	—	1260 s	1251 m	1251 m	1251 s
709 ms	663 s	649 ms	642 s	1390 s	1378 s	1376 s	1376 s
—	743 m	—	730 m	1456 m	—	—	—
764 vs	764 vs	762 vs	763 vs	1508 ms	1500 ms	1500 m	1495 s
792 vs	791 vs	788 vs	787 vs	1576 ms	1562 m	1560 m	1555 ms
—	829 m	805 m	—	1600 ms	1589 m	1602 m	1590 m
874 m	851 m	—	856 m	1640 w	—	—	—
—	967 s	946 m	942 s	3080 m	3075 m	3080 m	3072 m

TABLE 4. *Infra-red frequencies of* β-*halogenonaphthalenes in Nujol mull.*

β-Fluoro-	β-Chloro-	β-Bromo-	β-Iodo-	β-Fluoro-	β-Chloro-	β-Bromo-	β-Iodo-
418 m	—	—	—	879 s	888 ms	887 m	—
453 m	—	—	—	896 m	—	—	896 m
470 ms	470 s	475 vs	475 vs	—	940 m	939 m	932 ms
		580 mw	567 mw	—	—	—	947 m
—	602 ms	—	—	960 ms	962 m	—	961 m
618 m	625 m	619 m	—	—	1074 ms	1063 ms	1056 w
—	639 m	—	—	1156 m	1127 m	1130 m	1126 m
662 m	—	—	—	1212 ms	—	—	—
706 s	—	—	—	1247 ms	—	—	—
749 vs	746 vs	743 vs	735 vs	1357 ms	1343 m	1343 m	1338 m
—	787 m	789 m	765 m	1438 m	—	1377 ms	—
813 vs	817 vs	812 vs	815 vs	1510 s	1500 m	1500 m	1496 m
—	—	832 ms	—	1578 s	1572 m	1587 ms	—
—	851 m	851 ms	—	1602 ms	—	—	1610 ms
858 s	861 s	860 ms	865 ms	1630 m	—	—	—

TABLE 5.

α-X	ω_4 Raman (Luther)	ω_4 infra-red	α-X	ω_4 Raman (Luther)	ω_4 infra-red
F	709	709	Br	651	650
Cl	665	663	I	—	642

McConnell and McClure (*J. Chem. Phys.*, 1953, **21**, 1296) have assigned the naphthalene a_g 512 fundamental the value 430 cm.$^{-1}$ in the first excited singlet state. However, work on the absorption spectra of the halogenonaphthalenes has revealed a frequency of the value about 470 cm.$^{-1}$ in the first excited singlet level of these compounds. Examination of the infra-red and Raman data shows only two vibrations, in this region, that do not change appreciably with substitution, *viz.*, the 473 and 512 of naphthalene. The 473 mode is non-totally symmetric in naphthalene and is not expected to appear strongly as a progression in the spectra of the halogenonaphthalenes. Furthermore, it should be lowered in value in the excited state, so that identification with the observed frequency is not very likely. The frequency, however, is satisfactorily explained in terms of the 512 mode of naphthalene and the evidence for the assignment of this vibration to the value 430 cm.$^{-1}$ in the excited state must be considered very weak.

EXPERIMENTAL

The infra-red spectra were obtained with a Perkin-Elmer 12C spectrometer with a 13-cycle amplifier, sodium chloride and potassium bromide prisms being used. Calibration was effected in the normal manner, bands of water vapour, ammonia, and carbon dioxide being used for the sodium chloride region, and methanol vapour for the potassium bromide region.

Solids were examined as Nujol mulls, and pure liquids as capillaries between plates. The *cyclo*hexane solutions were 20% w/v, a 0·050-mm. cell being used for the sodium chloride region and a 0·20-mm. cell for the potassium bromide region.

The purity of the compounds has been reported elsewhere (Ferguson, *loc. cit.*; Ferguson, Iredale, and Taylor, *loc. cit.*).

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