Translated from *Uspekhi Khimii*, 53, 1959-1984 (1984) U.D.C. 535.3 + 541.6 + 547.024

The Vibrational Spectra of Neutral Free Radicals and the Corresponding Ions

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The results of studies on the vibrational spectra of simple and polyatomic neutral free radicals and the corresponding ions—the products of the one-electron reduction or oxidation of these radicals—are analysed.
The bibliography includes 157 references.

CONTENTS

I. Introduction 1139
II. The vibrational spectra of simple free radicals and their ions 1139
III. The vibrational spectra of polyatomic free radicals and the corresponding ions 1145

I. INTRODUCTION

Many chemical reactions proceed via a free-radical mechanism. The kinetics of such reactions are usually studied by EPR, which makes it possible to follow the time course of the reaction. However, in many instances the radicals can react without the involvement of the unpaired electron, which makes it difficult to follow the reactions of the radicals using EPR spectra. In such cases a detailed study and interpretation of the vibrational spectra of the intermediate radicals are necessary. The results of such studies for neutral and charged radicals have been surveyed.[1]

The extensive published experimental data show that, depending on the nature of the reacting substances, the free radicals can manifest a dual reactivity: on interaction with reductants and oxidants, they can respectively accept and give up an electron to form an anion or cation. Ionic reactions are known to play a significant role in organic processes and the investigation of the structures of ionic species is therefore extremely important. In the present review the vibrational spectra of free radicals and the corresponding ions are compared and certain considerations are put forward concerning the changes in the structure of the species as a consequence of the loss or addition of an electron. The influence of the protonation of molecules related to the radicals on their structure and vibrational spectra is also analysed.

II. THE VIBRATIONAL SPECTRA OF SIMPLE FREE RADICALS AND THEIR IONS

Simple free radicals and ions are extremely unstable and their detection by vibrational spectroscopy therefore involves considerable difficulties. Most studies employ the method of matrix isolation, whereby it is possible to detect free radicals and ions. There exists also another possibility for the investigation of the vibrations of short-lived molecular systems—the high speed recording of spectra; however, in view of its technical complexity it has been much less used.

Non-empirical calculations of the potential curves for the ground and excited electronic states of the $OH^{\cdot}$ radical and the ground state of the OH^{+} cation have been carried out[2] by the method of configuration interaction using pseudo-natural orbitals in terms of the approximation of bound electron pairs. The results agree with the experimental values listed in Table 1.

Table 1. The vibrational spectra and geometrical parameters of a series of simple molecules, radicals, and ions.

Species	ν, cm^{-1}	r, Å	α, °	$10^{-2}F_r$, Nm^{-1}	Refs.
OH^-	3570	—	—	—	[3]
$OH^{\cdot}$	3567[a]	0.971	—	—	[2]
$(OH^{\cdot})^*$	2689[a]	1.004	—	—	[2]
OH^+	2955	1.029	—	—	[2]
H_2O	3657 (asym.); 3756 (sym.)	0.957	105.2	7.66	[9]
H_3O^+	2600 (asym.); 3200 (sym.)	1.011	110.4	4.03—3.96	[9, 10]
NH_2^-	—	1.032	102.4	5.82	[17, 18]
$NH_2^{\cdot}$	3220	1.024	103.3	5.61	[11—14]
$(NH_2^{\cdot})^*$	3325	0.975	180	—	[13]
NH_2^+	2721 (asym.); 2822 (sym.)	1.03	108.7	4.68	[15, 16]
NH_3	3336 (asym.); 3414 (sym.)	1.017	107.8	6.16	[13, 16, 19]
NH_4^+	3040 (asym.); 3145 (sym.)	—	109.5	5.42	[17, 19]
PH_2^-	—	1.466	93.7	3.40	[24]
$PH_2^{\cdot}$	2270±80	1.442	94.6	7.26	[20, 23, 24]
PH_2^+	—	1.419	120.5	7.90	[24]
NO_2^-	1355[b]	1.286	—	—	[32]
$NO_2^{\cdot}$	1876[b]	1.151	—	—	[25, 27]
NO_2^+	2220; 2320—2340	1.062	—	—	[27—31]
NO_2^-	1315 (asym.); 1182 (sym.)	—	109	—	[33—35]
$NO_2^{\cdot}$	1329 (asym.); 1633 (sym.)	—	140.9; 126.1	—	[36—38]
NO_2^+	1400 (asym.); 2360 (sym.)	—	180	—	[19]
NS^-	1210	1.469	—	10.33	[41, 45, 46]
NS^+	1415	1.439	—	12.65	[41, 44, 45]
PO^-	1000	1.540	—	—	[23]
$PO^{\cdot}$	1218	1.476	—	—	[47]
ClO^-	713	—	—	3.3	[83]
$ClO^{\cdot}$	850	—	—	4.66	[83]
ClO_2^-	789.7 (asym.); 823.4 (sym.)	1.57	108.5	4.11	[77, 80]
$ClO_2^{\cdot}$	947.6 (asym.); 1104.5 (sym.)	1.472	112.2	6.61	[77, 79]
ClO_3^-	936	1.46	108	6.62	[78, 81]
$ClO_3^{\cdot}$	855 (asym.); 815 (sym.)	—	110; 112	—	[81]

Notation: ν is the vibration frequency, r is the equilibrium distance, α the angle between the bonds, F_r the force constant, ω_e the normal vibration frequency for infinitesimal amplitudes, and $\omega_e\chi_e$ the anharmonicity constant. The asterisk denotes excited states.

[a] Obtained from $\omega_e = 3740\ cm^{-1}$, $\omega_e\chi_e = 86.4\ cm^{-1}$ and $\omega_e = 3181\ cm^{-1}$, $\omega_e\chi_e = 95.9\ cm^{-1}$ for $OH^{\cdot}$ and $(OH^{\cdot})^*$ respectively.[2]

[b] Calculated from $\omega_e = 1904\ cm^{-1}$, $\omega_e\chi_e = 14\ cm^{-1}$ and $\omega_e = 1371\ cm^{-1}$, $2\omega_e\chi_e = 16\ cm^{-1}$ for $NO^{\cdot}$ and NO^- respectively.[27,32]

From the analysis of the literature data on the infrared and Raman spectra of the hydroxides MOH (M = Li, Na, Rb, or Cs) and $M(OH)_2$ (M = Mg, Ca, Sr, or Ba) as well as their hydrates at 95 and 295 K, Lutz et al.[3] concluded that the frequency of the stretching vibration of the unperturbed OH^- ion is 3570 ± 10 cm^{-1}. This value differs appreciably from that usually adopted (3700 cm^{-1}). The formation of the cation decreases the vibration frequency of the O–H bond, while the latter hardly changes on formation of the anion. Since the OH^+ cation has a triplet ground state,[2] i.e. its formation involves the abstraction of an electron from the unshared pair, the observed weakening of the bond is due to the displacement of electron density from the bond to the oxygen atom. At the same time the vibration frequencies of the OH^- anion and the OH· radical are identical, which suggests that the electron which reduces the radical to the anion occupies a non-bonding orbital.

The infrared and Raman spectra of the oxonium ion H_3O^+ have been studied in a number of investigations.[4–8] The following assignment of the frequencies in the spectrum of the H_3O^+ ion has been adopted assuming a symmetrical pyrimidal structure: the symmetrical deformation (ν_2) at 1100 cm^{-1}, the antisymmetric deformation (ν_4) at 1700 cm^{-1}, the antisymmetric stretch (ν_3) at 2400 cm^{-1}, and the symmetrical stretch (ν_1) at 3200 cm^{-1}. The constants calculated using the valence bond approximation[9] describe satisfactorily the experimental data. The significantly lower force constant of the O–H bond in H_3O^+ compared with the value obtained in terms of the same approximation for H_2O (Table 1) is associated with the increase of the interatomic distance by 0.054 Å as a consequence of the shift of electron density to the O–H bond newly formed on protonation of the water molecule. On the basis of the analogous change in the equilibrium distance by 0.055 Å in OH^+ relative to OH·, a similar change in the force constant may be expected also on formation of the OH^+ cation from the OH· radical.

Milligan and Jacox[11] were able to obtain the most complete vibrational spectrum of the $NH_2^·$ radical. The band at 1499 cm^{-1} was assigned to the ν_2 deformation, while that at 3220 cm^{-1} was assigned to the ν_3 antisymmetric stretch. In the study of the fluorescence excitation spectrum of the $NH_2^·$ radical the band at 3219 cm^{-1} was assigned[12] to the ν_1 symmetrical stretch. The experimental value of ν_2 for the deuterio-analogue is 1110 cm^{-1}. According to the authors,[11] the 16 cm^{-1} hypsochromic shift of the experimental deformation vibration frequency of $ND_2^·$ relative to the calculated value is caused by the difference between the contributions of the anharmonicity to the potential energies of the $NH_2^·$ and $ND_2^·$ radicals.

The excitation of the $NH_2^·$ radical is accompanied by a considerable increase of the angle α and a decrease of the bond length (Table 1). These changes are caused by the *sp* hybridisation of the N–H bond in the excited state, while in the ground state the N–H bond has a predominantly *p* character with a small contribution of the *s* orbital.[11] On ionisation of the $NH_2^·$ radical, the valence angle increases[15] as on its excitation, according to Milligan and Jacox,[11] this should be accompanied by a decrease of the bond length. However, the presence of the positive charge localised at the nitrogen atom apparently shifts the electron density from the bond to the N atom and lengthens the bond. There are no experimental literature data for the geometry of NH_2^+, but the results of a calculation[15] (Table 1) confirm the view that these competing effects exist. On protonation of the NH_3 molecule, the valence force constant of the N–H bond diminishes compared with the initial molecule (Table 1), while the deformation force constant hardly changes.[17] A significant difference between the frequencies of the deformation vibrations of ammonia (ν_2 = 930–970 cm^{-1} and ν_4 = 1628 cm^{-1})[19] and its protonated form (ν_2 = 1680 cm^{-1} and ν_4 = 1400 cm^{-1})[19] is then observed. A characteristic feature is that the homolytic rupture of the bond in both NH_3 and in H_2O (with formation of the radical) is accompanied by a lengthening of the corresponding bond and hence by its weakening compared with the initial molecule.

The deformation vibration frequency in the ground electronic state $^2B_1$ of the $PH_2^·$ radical is 1102 cm^{-1},[20] which agrees with the values quoted by Dixon et al.[21] and Berthou et al.[22] The stretching vibration frequency of $PH_2^·$ [20,23] and the equilibrium distances, angles, and force constants of the radical and the corresponding ions, calculated[24] by the non-empirical SCF LCAO MO method, are listed in Table 1. Analysis[23] of photoelectron spectroscopic data led to the conclusion that the geometry changes insignificantly following the abstraction of an electron from the PH_2^- anion, which agrees with other results.[24] The decrease of the force constant of the P–H bond in the sequence cation > radical > anion is apparently caused by the antibonding character of the successively added electrons.

Taking into account configuration interaction, calculations have been carried out by the SCF LCAO MO method for the three ($^2\Pi$) states of the NO· radical and the 19 ($^{1,3}\Sigma$, $^{1,3}\Pi$, and $^{1,3}\Delta$) states of the NO^+ ion.[25] The calculated vibration frequencies in the ground state are 1731 cm^{-1} for the radical ($^2\Pi$) and 1515 cm^{-1} for the cation ($^1\Sigma^+$). The experimental frequencies and equilibrium distances for the NO· radical and its ions are listed in Table 1. Evidently the calculated value for the radical is too low by 10% and that for the cation is too low by 30–35%. On the basis of the experimental data (despite the fact that a fairly considerable scatter of the vibration frequencies has been observed for the cation), one can conclude that the formation of NO^+ and NO· entails the abstraction of an electron occupying an antibonding orbital; in contrast to calculated data,[25] this should be accompanied by a significant increase of the frequency. The character and magnitude of the change in frequency on reduction of the radical show that the added electron is also in an antibonding orbital but a different one, because NO^- has a triplet ground electronic state.[32]

Table 1 lists the stretching vibration frequencies of the nitrite anion NO_2^- and the corresponding radical and cation. The antisymmetric stretching vibration band of the anion[33] is a doublet due to the Fermi resonance of the ν_1 vibration with the combination $\nu_3 + \nu_C(B_1)$, where $\nu_C(B_1)$ represents the libration of the anion. We may also note that the vibration frequencies of the $NO_2^·$ radical in the gaseous state[36] and in an argon matrix[37] are virtually identical and are satisfactorily described by the calculated data.[38] The significant decrease of the symmetrical stretching vibration frequencies in the cation–radical–anion series is associated, as in the previous case, with the antibonding character of the added electrons. Consequently the reduction and oxidation of the radical are apparently accompanied by a change in geometry. Indeed, the O–N–O angles have been determined[34] on the basis of the isotope shifts with respect to oxygen and nitrogen for $NO_2^·$ and with respect to oxygen for NO_2^- (Table 1). Evidently the formation of the anion entails a change in the hybridisation of the N–O bond from sp^2 to sp^3. Whereas both the anion and the radical have a bent conformation, the cation has a linear geometry,[19] which indicates *sp* hybridisation of the N–O bond, the existence of the cumulated bond system $O{-}\overset{+}{N}{-}O$, and the localisation of the positive charge at the nitrogen atom.

Using a gas cell with multiple reflection, ensuring a beam path length of 80 m, an infrared band at 1360 cm^{-1} has been obtained[39] and interpreted as due to the antisymmetric stretching vibration of the $NO_3^·$ radical. Having measured

the Raman spectra of the substances obtained on condensation of the NO_2–N_2O_4–Ne gas mixture onto a copper support at 9 K, Griffiths et al.[30] assigned the 1042, 1324, and 714 cm^{-1} bands respectively to the ν_1, ν_3, and ν_4 vibrations of the NO_2^- anion isolated in a neon matrix. These frequencies are close to the corresponding vibration frequencies of the nitrate anion in HNO_3 [39] and $M^+NO_3^-$.[40] Comparison of the above data suggests that the antisymmetric stretching vibrations of $NO_3^\cdot$ and NO_3^-, like those of $NO_2^\cdot$ and NO_2^- (Table 1), are insensitive to changes induced by the one-electron reduction of the radicals.

The results of non-empirical calculations of the geometry and force constants of $NS^\cdot$ and NS^+ in the ground state by the restricted SCF method are also presented in Table 1. For the radical, they agree well with the experimental data.[42] In the case of the cation the calculated equilibrium distance differs significantly from the value of 1.25 Å found[43] from the emission spectra. It has been suggested[41] that the experimental estimate of r_e(N–S) for the cation is too low. The observed higher vibration frequency of the bond in $NS^\cdot$ [44] compared with the radical,[45,46] as in the case of $NO^\cdot$ and NO^+, indicates the removal of the electron from an antibonding orbital.

The changes in the vibration frequency and equilibrium distance on one-electron reduction of the $PO^\cdot$ radical[47,48] are listed in Table 1. The similarity of the vibration frequency of the $PO^\cdot$ radical to that of the stretch of the P–O bond in HPO (1188 cm^{-1}) indicates the localisation of the unpaired electron mainly at the phosphorus atom. The addition of an electron to the radical leads to a considerable decrease of the bond vibration frequency, caused, as in the case of $NO^\cdot$, by the concentration of the negative charge on the oxygen atom. The observed change in the vibrational spectrum is due to the increase of the equilibrium distance in PO^- compared with the radical.

The fluorescence and excitation spectra of the $NCO^\cdot$ radical-ion isolated in an argon matrix have been obtained with the aid of a dye-based laser[48] (Table 2). The vibration frequencies ν_1 and ν_3 obtained agree well with infrared spectroscopic data,[49] while the frequency ν_2 proved to be higher by 42 cm^{-1}. The authors[48] indicated the presence of Fermi resonance between the ν_1 and $2\nu_2$ levels in the excited electronic state of $N\dot{C}O$. The reduction of the radical to the anion weakens the C–O bond (the ν_1 vibration) and strengthens the N–C bond (the ν_3 vibration) owing to the localisation of the negative charge on the oxygen atom. There are no experimental literature data for the vibrational spectra of the NCO^+ ion, while according to data calculated[53] by the SCF method for the NCO^+ linear system, the formation of the cation entails a decrease of the C–O internuclear distance and an increase of the N–C distance (Table 2). Since the cation has a triplet ground state,[53] its formation apparently involves the abstraction of an electron from the unshared electron pair of the nitrogen atom. The consequent presence of a positive charge on the nitrogen atom shifts the electron density from the bond to the nitrogen atom and lengthens the bond.

Table 2 presents the equilibrium distances and the frequencies and force constants for the $CN^\cdot$ radical and its ions. Analysis of the changes in the σ- and π-overlap energies[55] shows that the abstraction of an electron from the anion leads to the stabilisation of the σ-binding ($\Delta\Omega^\sigma = -0.40$) and to destabilisation of the π-binding ($\Delta\Omega^\pi = 0.57$), the influence of the latter effect being greater. According to the results of non-empirical calculations,[58] the CN^+ ion also has a triplet ground electronic state, which is indicated likewise by the character of the change in the equilibrium distance when the radical is converted into the cation. Presumably the vibration frequency of the cation is somewhat lower than that of the radical in the excited state.

The vibrational spectra of hydrogen dihalide free radicals (with $D_{\infty h}$ symmetry) and the corresponding anions have been investigated[59–65] (Table 3). In their study of the infrared spectra of the products, isolated in an argon matrix, of the interaction of Hal_2 and HHal (where Hal = Cl, Br, or I) in a discharge, Noble and co-workers[59–61] observed bands which were assigned to the ν_{sym} and ν_{asym} vibrations of the radicals $HHal_2^\cdot$ and $DHal_2^\cdot$. The presence in the spectrum of combined stretching vibration frequencies justifies the assumption that the anharmonicity of the bond vibrations is significant for the systems investigated. Indeed, the expressions for the potential energy of radicals of the type $HHal_2^\cdot$ include a large quartic term, which is responsible for the anharmonicity of the H–Hal bond vibrations, the contribution of the term diminishing sharply with increase of the size of the halogen atom.

Table 2. The spectroscopic characteristics and equilibrium distances of cyanate and cyanide ions and radicals.

Species	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	r_{CO}, Å	r_{NC}, Å	$10^{-2}F_r$, Nm^{-1}	Refs.
NCO^-	1210	627	2176	1.23	1.17	—	[50–52]
$NCO^\cdot$	1272	529	1923	1.18	1.23	—	[48]
NCO^+	—	—	—	1.125	1.468	—	[49]
NC^-	—	—	2080	—	1.14	16.4	[56, 57]
$NC^\cdot$	—	—	2042[a]	—	1.172	15.9	[54, 55]
$(NC^\cdot)^*$	—	—	1788[a]	—	1.23	—	[54]
NC^+	—	—	—	—	1.27	—	[58]

[a] Obtained from $\omega_e = 2068$ cm^{-1}, $\omega_e\chi_e = 13$ cm^{-1} and $\omega_e = 1813$ cm^{-1}, $\omega_e\chi_e = 13$ cm^{-1} for $NC^\cdot$ and $(NC^\cdot)^*$ respectively.

Analysis of the infrared and Raman spectra of HCl_2^- [62] and HBr_2^- [63] indicates a linear and centrosymmetric structure of the anions. The force constants obtained from the experimental data indicate insignificant changes in the force field following the abstraction of an electron from the non-bonding molecular orbital of the ions investigated. Comparison of the force constants for the $HHal_2^\cdot$–$HHal_2^-$ pairs leads to the conclusion that the contribution of the anharmonic term to the expression for potential energy is greater for the radical. The dependence of the contribution of this term on the size of the halogen atom for the ions is the same as for the radicals, but it is smoother. Thus the one-electron reduction of radicals of the type $HHal_2^\cdot$ has little influence on the strength of the hydrogen bond, but leads to an increase of the anharmonic character of the potential function. On the grounds that the HF_2^- spectrum is characterised by the vibration frequencies $\nu_{asym} = 600\,cm^{-1}$ and $\nu_{sym} = 1450\,cm^{-1}$ [64] or $\nu_{sym} = 1377$ cm^{-1},[65] Noble and co-workers[60] therefore suggest, in contrast to the calculated data,[66] that the radical $HF_2^\cdot$ should be stable.

The interaction of atomic fluorine with CF_2 in an argon matrix at 14 K made it possible[67] to obtain a concentration of the $CF_3^\cdot$ radicals sufficient (in contrast to another study[68]) for the detection of all four vibrations. This radical has the C_{3v} symmetry; its stretching vibration frequencies are listed in Table 3. On the basis of the results of the calculation, the authors[67] concluded that there is a Fermi resonance between the $\nu_2 + \nu_4$ and ν_3 vibrations in the $^{13}CF_3^\cdot$ spectrum and the force field parameters obtained indicate a pyramidal form for this radical. The angle of deviation from the plane is 13°, which has been confirmed by EPR data.[69]

Among the products of the photoionisation of CF_3X (where X = Cl, Br, I, or H), stabilised cations, previously detected (from the mass spectra) only in the gas phase, have been found in solid argon (Table 3).[70] The formation of these ions is accompanied by an increase in the frequencies of both the symmetrical and asymmetrical stretching vibrations. Particular mention should be made of the high antisymmetric stretching vibration frequency of the CF_3^+ cation due to the intense $(p-p)\pi$ interaction. On this basis, it has been concluded[70] that the difficulty of the stabilisation of the cation is caused by its high reactivity and not its "physical" instability. The low frequency of the experimental ν_{asym} band for the $^{13}CF_3^+$ cation compared with the calculated value (1612 cm^{-1}) has been explained[70] by the Fermi resonance between the $\nu_1 + \nu_4$ and ν_3 vibrations.

Table 3. Parameters of the infrared spectra of halogen-containing radicals and their ions.

Species	ν_{sym}, cm^{-1}	ν_{asym}, cm^{-1}	ν (C-X), cm^{-1}	Refs.
HCl_2^-	770	253	—	[62]
$HCl_2^{\cdot}$	696	260	—	[59]
DCl_2^-	520	225	—	[62]
$DCl_2^{\cdot}$	463.7	265.2	—	[59]
HBr_2^-	670	170	—	[63]
$HBr_2^{\cdot}$	727.4	164.7	—	[60]
DBr_2^-	550	160	—	[63]
$DBr_2^{\cdot}$	469.1	169.6	—	[60]
$HI_2^{\cdot}$	682.1	120.7	—	[61]
$DI_2^{\cdot}$	470	124	—	[61]
$CF_3^{\cdot}$	1087	1251	—	[67]
CF_3^-	1125	1667	—	[70]
$^{13}CF_3^{\cdot}$	1063	1219	—	[67]
$^{13}CF_3^+$	—	1600	—	[70]
$CF_2Cl^{\cdot}$	1208	1148	761	[70]
CF_2Cl^+	1515	1415	—	[70]
$CF_2Br_2^{\cdot}$	1197	1137	685	[70]
$CF_2Br_2^+$	1484	1368	—	[70]
$CF_2I^{\cdot}$	1190	1126	627	[70]
CF_2I^+	1433	1321	—	[70]
CF_4	908	1280	—	[19]

Since only the intense antisymmetric stretching vibration band is manifested in the infrared spectrum of the radical $CCl_3^{\cdot}$ [71] (Table 4) and the symmetrical stretching vibration band is absent, it has been suggested[72] that the radical has a planar structure (D_{3h} symmetry). However, the results of a non-empirical calculation[73] and EPR data[74] indicate a pyramidal structure. Table 4 lists the force constants for both the planar and pyramidal structures. On irradiation (λ = 1216 Å) of chloroform molecules isolated in an argon matrix at 14 K, CCl_3^+ cations have been obtained at a concentration sufficient for the investigation of their infrared spectra [72] (Table 4). The decrease of the force constant on passing from the cation to the radical demonstrates, as for $CF_3^{\cdot}$, the antibonding character of the unpaired electron. It is of interest to note that in the case of the CCl_4 molecule a further decrease of the antisymmetric stretching vibration frequency (force constant) and an increase of the deformation vibration frequency take place (Table 4).

Carver and Andrews[75] carried out the simultaneous deposition of chloroform and lithium vapour onto caesium iodide windows at high dilution in argon at 15 K and obtained bands in the spectrum of the product which were assigned to $HCCl_2^{\cdot}$ vibrations (Table 4). Postulating, by analogy with radicals of the type $CHal_3^{\cdot}$, that the unpaired electron in $HCCl_2^{\cdot}$ promotes the formation of a pyramidal structure, the authors[75] assumed that the H–C–Cl and Cl–C–Cl angles are 115°. The infrared spectra of matrix-isolated ions corresponding to the $HCCl_2^{\cdot}$ radical have been investigated.[72] A planar structure (C_{2v} symmetry) in the ground electronic state has been proposed for the $HCCl_2^+$ cation, as in the case of CCl_3^+. The addition of an electron to the $HCCl_2^{\cdot}$ radical leads to the formation of the anion $HCCl_2^-$, which has a pyramidal structure with still smaller valence angles. As for the isoelectronic H_2CCl_2 molecule, the angles in the anion are therefore assumed to be tetrahedral. The valence and deformation force constants obtained from these data are listed in Table 4. Evidently the force constant of the C–Cl bond gradually diminishes as each succeeding electron is added, which corresponds to a decrease of the strength and an increase of the length of the bond (from 1.70 Å for the cation to 1.75 Å for the anion). The deformation force constant depends on the valence angle, while the interaction constant hardly changes in the cation–radical–anion series.

Table 4. Parameters of the infrared spectra and force constants of certain chloro- and bromo-methanes.

Species	ν_{asym} (C-Hal), cm^{-1}	δ, cm^{-1}	α, °	$10^{-2}F_r$, Nm^{-1}	$10^{-2}F_\alpha$, Nm^{-1}	Refs.
$CCl_3^{\cdot}$	898	200*	116	3.1; 3.4	—	[71, 74]
CCl_3^+	1037	150–200*	120	3.8–3.9	—	[72]
CCl_4	790	314	109.5	3.08	—	[75]
$HCCl_2^-$	837.6	1270	109.5	3.27	0.76	[72]
$HCCl_2^{\cdot}$	902	1226	115; 120	3.75; 3.48	0.64; 0.48	[72, 75]
$HCCl_2^+$	1038	1291	120	4.65	0.52	[72]
$CBr_3^{\cdot}$	773	—	—	3.55	—	[76]
CBr_3^+	874	—	—	—	—	[65]
CBr_4	675	—	—	2.45	—	[76]

Notation: δ is the deformation vibration frequency and F_α the deformation vibration force constant; the remaining notation is the same as in Table 1.
*Postulated deformation vibration frequencies.

The formation of the tribromomethyl cation induces, as for CCl_3^+, an increase of the antisymmetric stretching vibration frequency (Table 4) compared with the radical. Whereas the frequency change for the trichloromethyl and tribromomethyl cations is 100–150 cm^{-1}, the corresponding value for the trifluoromethyl cation under these conditions (Table 3) is 400 cm^{-1}. The greater amount of double bond character in the $CCl_3^{\cdot}$ and $CBr_3^{\cdot}$ radicals relative to CCl_4 and CBr_4 is associated, according to the authors,[75,76] with the $(p-d)\pi$ interaction, the strength of which increases greatly for planar structures, i.e. for cations. On the other hand, following the homolytic dissociation of the C–F bond in CF_4, the asymmetric stretching vibration band (Table 3) undergoes a bathochromic shift, in contrast to $CCl_3^{\cdot}$ and $CBr_3^{\cdot}$, apparently owing to the absence of *d* orbitals.

Tevault et al.[77] investigated the infrared and Raman spectra and determined the parameters of the force field of the chlorite anion ClO_2^- and the corresponding $ClO^{\cdot}$ radical (Table 1). The calculated force constant of the Cl–O bond for the anion is much smaller than for the radical. The

results of a calculation[78] by the LCAO MO method, including the 3*d* orbitals of chlorine, predict for $ClO_2^{\cdot}$ that the π-bond order of the bond having 50% *d* character is 0.75, while that of the bond having total *d* character in ClO_2^- is 0.13. The higher π-bond order in $ClO_2^{\cdot}$ agrees with the greater bond force constant. Bearing in mind that only the *p* orbitals of the atoms are involved in the formation of molecular orbitals, one may conclude that the electron adding to the radical in the anion should occupy an antibonding molecular orbital which diminishes the $(p-p)\pi$ bond order. Both the lower valence force constant in the anion and the greater bond length agree with the antibonding character of the added electron. Tevault et al.[77] calculated the change in the O–Cl–O angle (Table 1) from the shift of the symmetrical stretching vibration frequency on isotope substitution of ^{35}Cl by ^{37}Cl, the result agreeing with the values found in other studies.[79,80]

The resonance Raman scattering (λ_{exc} = 6328 and 5145 Å) and the infrared spectra of the $ClO_3^{\cdot}$ radical formed on irradiation of $NaClO_3$ crystals by electrons having an energy of 15 MeV (T = 77 K) have been investigated[81] (Table 1). It was observed that the radical in the $NaClO_3$ lattice occupies two translationally non-equivalent positions, which leads to the splitting of the observed bands ($\Delta\nu$ = 5–7 cm^{-1}). Apart from the frequencies assigned to the vibration of the $^{35}ClO_3^{\cdot}$ radical, a band is shown in the infrared spectrum, which can be assigned to the ν_{sym} vibration of the $^{37}ClO_3^{\cdot}$ radical. However, the O–Cl–O angle obtained on this basis, which amounts to 100°, is lower than the value (112°) calculated from the EPR spectra.[82] The band at 936 cm^{-1} has been attributed to the symmetric ClO_3^- vibration, which is consistent with other data.[19] The anion under consideration has a pyramidal structure; its geometrical parameters and the valence force constants are given in Table 1. According to Wagner,[78] the ClO_3^- anion is characterised by a Cl–O bond whose π-bond order is 0.28 and which is fully of the *d* type.

In the photolysis of a Cl_2–O_2 mixture the infrared spectrum of the products showed (a multireflection gas cell with an optical length of 80 m was used) a band at 942 cm^{-1}, which was assigned[83] to the vibration of the short-lived $ClO^{\cdot}$ radical. This value is close to that (Table 1) obtained from the Raman spectra of the $ClO^{\cdot}$ radical isolated in the argon matrix. The vibrational frequency (850–1030 cm^{-1}) and force constants [$(4.8–6.9) \times 10^2$ N m^{-1}] for this radical has been calculated[78] by the method of "atoms in the molecule". The low vibrational frequency of the ClO^- anion (Table 1) indicates the localisation of the negative charge on the oxygen atom, which is confirmed by the absence of a π-component of the bond in it.[78] On the other hand, the radical has a π-bond order of 0.5 (a bond having 100% *p* character). The involvement of the *d* orbital, responsible for the electron-accepting properties, increases in the sequence[78]

$$ClO^- < ClO^{\cdot} < ClO_2^- < ClO_2^{\cdot} < ClO_3^- < ClO_4^-$$

In analysing this sequence, one can assume that the electron-accepting capacity of $ClO_3^{\cdot}$ is greater than that of ClO_3^-. However, sometimes (and the antibonding character of the outer molecular orbital of the systems of the type ClO_n considered agrees with this) the stretching vibration frequencies of the $ClO_3^{\cdot}$ radical should appear in a higher range than those of its anion. This conflicts with the results of Bates and Stidham.[81] The discrepancy with these data can be accounted for by the influence of the crystal field of $NaClO_3$, whose effect is apparently different for the radical and the anion.

The vibrational spectra of the methyl radical $CH_3^{\cdot}$ both in solid inert gas matrices and in the gaseous state have been investigated in a number of studies.[84–87] The most complete infrared spectrum has been described by Snelson[84] (Table 5). A stretching vibration frequency ν_1, not shown in the infrared spectrum, has been predicted. The force field parameters obtained for the radical agree well with the experimental data. The discrepancy between the calculated and experimental frequencies for $CD_3^{\cdot}$ is due to the influence of the anharmonicity[84] and is not a result of the interaction of the radical with the matrix. In the ground electrostatic state the methyl radical has a planar[85,86] or quasi-planar[88] structure.

The methyl anion CH_3^- has been generated in the gas phase; its photoelectron spectrum has been obtained with a well resolved vibrational structure, whereby it is possible to determine the deformation vibration (umbrella motion) frequency[88] (Table 5). It was concluded that the CH_3^- anion has a pyramidal structure, which agrees with data for anions of the type $CHal_3^-$. The methyl cation CH_3^+ has a planar structure and the equilibrium distance (Table 5) suggests that its stretching vibration frequencies should have undergone bathochromic shift compared with the radical and should appear close to the stretching vibrations of methane.

Table 5. Parameters of the infrared spectra and equilibrium distances in the molecules of methane and its derivatives.

Species	ν_1, cm^{-1}	δ_2, cm^{-1}	ν_3, cm^{-1}	δ_4, cm^{-1}	*r*, Å	Refs.
CH_3^-	—	460	—	—	—	[88]
$CH_3^{\cdot}$	3044	617	3162	1398	1.079	[84–86, 88]
$CD_3^{\cdot}$	2153	463	2381	1026	—	[84]
CH_3^+	—	—	—	—	1.091; 1.120	[90, 91]
CH_4	2916	—	3019	—	1.094	[89]

A series of studies of the structure and infrared spectra of alkyl radicals merit attention.[92–95,105,109] Pacansky and Dupuis[93] investigated the vibrations of the bonds and angles in the ethane–ethyl radical–ethylene series, which enabled them to interpret the infrared spectrum of the ethyl radical and its deuterio-analogue. The geometrical parameters calculated by the non-empirical SCF method were used in the calculation. The infrared bands of the ethyl radical $C_2H_5^{\cdot}$ can be assigned to the vibrations of the methyl and methylene groups in ethane and ethylene respectively. It has been noted that the infrared spectrum of this radical shows a number of characteristic features. Thus the low (2842 cm^{-1}) stretching vibration frequency of the β-CH bond, which shields the unpaired electron orbital, is caused[93] by the weak interaction of this bond with the radical centre (Table 6). This is the longest bond in the methyl group.[95] The appreciably lower frequency of the pyramidal deformation vibration of the CH_2 group in the ethyl radical compared with the corresponding vibrations for ethylene is induced by the absence of a π-bond in the ethyl radical and hence by the facilitation of movement of the "pyramidal" type. The broadening of the band due to this vibration is associated with the complex movement (inversion against the background of the internal rotation about the C–C bond) executed by the radical centre. The stretching vibration frequencies of the CH_2 group and the hypsochromic shift of the bands corresponding to the vibrations of the O–C bond in the radical relative to the frequency of the corresponding ethane band indicate a greater strength of all the bonds in the radical fragment; the lengths of these bonds are reduced, which has been confirmed by calculations.[95] Analogous changes have been observed in the methyl radical relative to methane

(Table 5). On the basis of results calculated by the non-empirical SCF LCAO MO method using an extended basis set of Gaussian functions, it has been shown that the formation of the $C_2H_5^+$ cation is accompanied by a further decrease of the length of the C–C bond (Table 6), which apparently entails an increase of its stretching vibration frequency. The carbon atom in the methylene group is sp^2-hybridised, that in the methyl group is sp^3-hybridised, and the HCCH angle is 90°.

Table 6. Parameters of the vibrational spectra and bond lengths of the ethyl radical, the related molecules, and the cation.

Species	Methyl group		Methylene group			ν (C–C), cm^{-1}	r_{CC}, Å	Refs.
	ν (C–H), cm^{-1}	r_{CH}, Å	ν_{sym} (C–H), cm^{-1}	ν_{asym} (C–H), cm^{-1}	δ, cm^{-1}			
H_3C-CH_3	2954	1.102	—	—	—	1016	1.528	[93]
$H_3C-\dot{C}H_2$	2920; 2842	1.076; 1.090	3033	3112	540	1175	1.498	[93]
$H_3C-CH_2^+$	—	—	—	—	—	—	1.48	[91]
$H_2C=CH_2$	—	—	3026; 2989	3106; 3103	949	1623	1.34	[93, 109]

Jackels[96] calculated in terms of the harmonic approximation the vibration frequencies for the methoxy-radical $CH_3O^\cdot$ (Table 7). The values obtained agree well with the experimental data.[97–99]

It has been observed[96] that the C–O bond vibration in the ground state of $CH_3O^\cdot$ has the characteristic value, while in its deuteriated analogue there is a strong interaction of the deformation vibration of the DCO angle with the stretching vibration of the C–O bond. The stretching vibration frequencies of the C–O bond in the excited state, amounting to 678 cm^{-1} for $CH_3O^\cdot$ and 655 cm^{-1} for $CD_3O^\cdot$, have been determined from the fluorescence excitation spectra.[98] In conformity with the results of the calculations[100,101] (Table 7), the formation of the CH_3O^- anion entails an increase of the C–H bond length and the HCO angle and a decrease of the C–O bond length and the HCH angle. The decrease of the C–O bond length is somewhat unexpected, since the formation of an anion from oxygen-containing radicals, for example $NCO^\cdot$, leads to a decrease of the C–O bond vibration frequency, i.e. to an increase of the bond length compared with the radical.

In the methoxide anion the C–O bond length should apparently also increase relative to the $CH_3O^\cdot$ radical, but, since the substituents at the carbon atom are hydrogen atoms, the increase is smaller than for NCO^- and $NCO^\cdot$. Only the deformation vibration of the methyl group, whose frequency has undergone an appreciable bathochromic shift relative to the methyl radical, could be observed for CH_3O^- on the basis of photoelectron spectroscopic data.[102] A quantum-chemical analysis showed[103] that CH_3O^+ has a triplet ground state. On the other hand, according to Bouma et al.,[104] the methoxy-cation is unstable in the singlet state and undergoes the non-activated transition to the hydroxymethyl structure $HOCH_2^+$. In the triplet state the structure of CH_3O^+ is locally stable and has an energy higher by 387 kJ mol^{-1} than that of the singlet $HOCH_2^+$. Thus the formation of the CH_3O^+ cation is associated with the abstraction of an electron occupying a non-bonding orbital in the radical.

Using the second harmonic of a tunable dye laser (310–360 nm), Inoue et al.[105] obtained the excitation and fluorescence spectra of $C_2H_5O^\cdot$. The characteristics of the spectra of the ethoxy-radical are similar to those observed for $CH_3O^\cdot$. Since $C_2H_5O^\cdot$ contains the C–C–O fragment, the similarity of the force constants and the atomic weights of carbon and oxygen leads to the interaction of the C–C–C–O bond vibrations in the ground state. The vibration frequency obtained from the fluorescence spectra, amounting to 1067 cm^{-1}, is therefore associated with the stretching vibration of the C–C–O$^\cdot$ skeleton, in contrast to $CH_3O^\cdot$. According to the results of a non-empirical calculation by the same workers,[105] the 1063 cm^{-1} frequency, which virtually agrees with the experimental value (Table 7), refers to the out-of-phase skeletal stretching vibration of $C_2H_5O^\cdot$ in the ground state, while the 939 cm^{-1} frequency refers to the in-phase vibration. The fact that the frequency of the out-of-phase stretching vibration in $C_2H_5O^\cdot$ is higher than the frequency of the corresponding vibration of $CH_3O^\cdot$ in the ground state agrees with the observed difference between these frequencies for ethyl and methyl alcohols (Table 7). The stretching vibration frequency of the C–O bond in the $C_2H_5O^\cdot$ radical in the excited state is much smaller, as in the case of $CH_3O^\cdot$, than for the ground state. Pinchas[106] gives C–O$^-$ (C–C–O$^-$) bond stretching vibration frequency of the ethoxide anion $C_2H_5O^-$ a value which hardly differs from that of the corresponding vibration in the radical. This agreement may be associated with the fact that the electron which reduces the radical to the anion occupies a non-bonding orbital with the unpaired electron; the anion must then have a singlet electronic ground state.

Table 7. The vibration frequencies and geometrical parameters of the molecules of methanol and ethanol and their derivatives.

Species[a]	ν (CH3), cm^{-1}	r_{CH}, Å	ν(CO), cm^{-1}	r_{CO}, cm^{-1}	$\delta(CH_3)$, cm^{-1}	α (HCH), °	α (HCO), °	ρ_r, cm^{-1}	Refs.
CH_3O^-	—	1.12	—	1.35; 1.39	1075	102.9	114	—	[100–102]
$CH_3O^\cdot$	3118	1.112	1017	1.405	1330	109.1	111.3	690	[96]
$(CH_3O^\cdot)^*$	—	—	678	—	—	—	—	—	[98]
CH_3OH	2989; 2943; 2835	1.096	1033	1.427	1448	109.2	—	—	[109]
$C_2H_5O^-$	—	—	1068	—	—	—	—	1118	[106]
$C_2H_5O^\cdot$	—	—	1067	—	—	—	—	—	[105]
$(C_2H_5O^\cdot)^*$	—	—	596	—	—	—	—	—	[105]
C_2H_5OH	—	—	1050	—	—	—	—	1095	[106]

[a] The asterisk denotes excited states.

The infrared spectrum of the isopropyl radical in an argon matrix shows[107] four groups of bands (Table 8). The out-of-plane deformation vibration frequency of the radical centre is virtually identical with the value 380 ± 18 cm^{-1} obtained from EPR data.[108] Many observed bands are doublets, which can be accounted for[107] by the existence of more than one conformation of the isopropyl radical. The manifestation of the stretching vibration of the α-CH bond of the radical in the region corresponding to the vibrations of the CH bonds of olefin molecules enabled the authors[107] to conclude that the bond length and the force constant of the radical centre are the same as in olefinic hydrocarbons. This conclusion has been confirmed by the results of a non-empirical SCF LCAO MO calculation. The low frequency of the out-of-plane deformation vibration band of the radical compared with the corresponding vibration of propene[109] shows that the p^2-hybridised carbon atom in the radical consumes less energy on the movement of the "pyramidal" type owing to the absence of the π-bond. We may note that the abstraction of an electron from iso-$C_3H_7^\cdot$ is accompanied by a decrease of the stretching vibration frequency and an

increase of the C–H bond length in the methyl groups (Table 8). The bond lengths in the methyl groups in the pairs $CH_3^{\cdot}$–CH_3^+ and $C_2H_5^{\cdot}$–$C_2H_5^+$ change similarly (Tables 5 and 6). By analogy with the variation of the C–C equilibrium distance (in the C_2H_6–$C_2H_5^{\cdot}$–$C_2H_5^+$ series) (Table 6), one may expect that the C–C bond length in the isopropyl cation is smaller than in the radical which conflicts with the data of Alah et al.[110] It may be that the cause of the 100 cm^{-1} difference between the calculated and experimental asymmetric stretching vibration frequencies of the C–C bond (Table 8) for the cation is the unduly high value of r_{CC} used in the calculation.

Table 8. The vibration frequencies and geometrical parameters of the isopropyl and t-butyl radicals and their cations.

Species	$\nu(\alpha$–CH), cm^{-1}	ν (C–H) in CH_3, cm^{-1}	r_{CH} in CH_3, Å	δ (CH_3), cm^{-1}	δ_π, cm^{-1}	ν (C–C), cm^{-1}	r_{CC}, Å	α (CCC), °	Refs.
CH_3–$\dot{C}H$–CH_3	3060	2900–2800	1.086–1.090	1500–1390	369	—	1.498	—	[107]
CH_3–$\overset{+}{C}H$–CH_3	—	2730	1.11	1499	—	1260	1.50	—	[110]
CH_3–$\dot{C}H$–CH_3	—	2870–2960	1.085	—	578	920	1.501	—	[109]
$(CH_3)_3C^{\cdot}$	—	2931; 2825	1.084; 1.091	1455; 1370	—	992; 733	1.502	118.4	[111]
$(CH_3)_3C^+$	—	2830	1.11	1455	—	1290	1.500	120	[110]

Notation: $\nu(\alpha$–CH) is the stretching vibration frequency of the C–H bond which does not shield the unpaired electron orbital in the radical and δ_π represents the out-of-plane deformation vibration.

The infrared spectrum of the t-butyl radical has been interpreted by Pacansky and Chang[111] (Table 8). As for $C_2H_5^{\cdot}$ and iso-$C_3H_7^{\cdot}$, the lengths of the C–H bond in the methyl groups of $(CH_3)_3C^{\cdot}$, which shield the unpaired electron, is greater than the C–H bond lengths in other CH_3 groups. In contrast to the radical, the central $(CH_3)_3C^+$ fragment has a planar structure. The vibrational frequencies of the cation, calculated using the geometrical parameters (Table 8), are virtually identical with the experimental data.

Thus the regularities in the variation of the stretching vibration frequencies and bond lengths for the t-butyl radical and its cation are the same as for the alkyl radicals and their cations presented above: the abstraction of an electron from the radical is accompanied by an increase of the vibration frequency of the bonds (by a decrease of bond lengths) of the fragment losing the unpaired electron and by a decrease of the stretching vibration frequencies (i.e. by an increase of the C–H bond lengths) of the methyl groups.

III. THE VIBRATIONAL SPECTRA OF POLYATOMIC FREE RADICALS AND THE CORRESPONDING IONS

The fluorescence and fluorescence excitation spectra of the cyclohexadienyl radical $C_6H_7^{\cdot}$ (at a concentration of 10^{-3} mole % relative to that of the initial molecules), obtained on irradiation of polycrystalline benzene and deuteriobenzene by fast electrons (energy 9 MeV, dose 10^7 rad) at 77 K, have been investigated[112] at 4.2 K. The source of excitation of the fluorescence was a UV-1000 nitrogen laser. Treating the radical as a benzene "molecule", the authors assigned the fluorescence lines at 5586 and 5516.5 Å to the 0–0 transition in $C_6H_7^{\cdot}$ and $C_6D_7^{\cdot}$ respectively. The shift of the absorption lines for the deuteriated specimen was 139 cm^{-1}. The vibrational frequencies of the ground and excited states of $C_6H_7^{\cdot}$ and $C_6D_7^{\cdot}$ are close to those of the corresponding benzene vibrations. On the basis of the frequency shift on deuteriation, the authors assigned the 552, 1169, and 1566 cm^{-1} bands in the spectrum of the cyclohexadienyl radical to the ν_6, ν_9, and ν_8 (C_{2g}) vibrations (Wilson's numbering).

Perkampus[113] investigated the infrared spectra of deposited films of salts having the composition ArH–HX–MX_3 (where ArH = benzene or methylbenzene and MX_3 = $AlCl_3$, $AlBr_3$, $GaCl_3$, or $GaBr_3$) at low temperatures. The nature of MX_3 does not exert a significant influence on the spectrum of the complex. The observed spectra differ appreciably from those of the aromatic hydrocarbons ArH and have been attributed to the carbonium salts $ArH_2^+MX_4^-$. The absorption bands of the anions AlX_4^- and $Al_2X_7^-$ have been detected in the infrared spectra of the complexes,[114] which serves as additional evidence for the ionic structure of the complexes: $ArH_2^+AlX_4^-$ and $ArH_2^+Al_2X_7^-$. The addition of a proton to ArH alters the symmetry of the aromatic ring (from D_{6h} for benzene to C_{2v} for the complex), as a result of which some of the bands, which are forbidden for the initial hydrocarbon, appear in the spectrum of the adduct. For example, the 1595 cm^{-1} band, observed in the spectra of substituted benzene derivatives, has been interpreted as due to the skeletal vibration of the C=C bond. On the basis of these considerations and taking into account the influence of the substitution of hydrogen by deuterium on the spectra, the vibration frequencies of the $C_6H_7^+$ ion were assigned[113] (Table 9). The new band at 640 cm^{-1}, observed in the spectrum of the benzene complex, corresponds to the 490 cm^{-1} band in the spectrum of its deuterio-analogue. The relatively large isotope shift enabled the authors to assign this band to a vibration of the C–H bond.

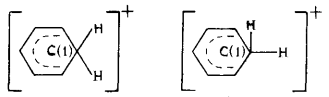
Table 9. Assignment of the bands in the infrared spectrum of $C_6H_7^+$.

Vibration (after Wilson)	Symmetry	ν, cm^{-1}		Vibration mode	ν, cm^{-1}
		C_6H_6	$C_6H_7^+$ [113]		$C_6H_7^{\cdot}$ [112]
$\nu_{8a,\ b}$	E_g^+	1596	1595 s.; 1580 v.w.	β(CCH), Q(CC)	1566
ν_{19}	E_u^-	1485	1445 v.s.	β(CCH), Q(CC)	—
ν_3	A_{2g}	1326	1328 v.w.	β(CCH)	—
ν_9	E_g^+	1178	1205 m.	β(CCH), Q(CC)	1169
ν_{15}	B_{2u}	1146	1178 s.	β(CCH), Q(CC)	—
ν_5	B_{2g}	985	983 v.w.	ρ(C–H), $\varkappa$(CCC)	—
ν_{17}	E_u^-	970	953 w.	ρ(C–H), $\varkappa$(CCC)	—
ν_1	A_{1g}	992	901 m.; 814 m.	Q(CC)	—
ν_{11}	A_{2u}	671	690 v.s. 640 v.s.	ρ(C–H)	—
ν_6	E_g^+	606	881 w.	γ(CCC)	552

Notation: s. = intense (strong) absorption band, v.w. = very weak band, v.s. = very intense band, w. = weak band, and m. = moderately intense band.
Note. The numerals in square brackets denote references (Ed.of Translation).

A similar study has also been carried out for methylbenzenes.[115] The spectra were interpreted on the assumption that σ-complexes are formed in which the proton adds to one of the carbon atoms of the aromatic ring via a σ-bond

produced by two electrons from the aromatic sextet localised in a hybrid sp^3 orbital of the carbon atom. In the limiting case both hydrogen atoms at C(1) are equivalent and are disposed symmetrically relative to the plane of the ring [structure (I)]:



(I) (II)

However, Bystrov[116] drew attention to the great similarity between the spectra of the σ-complex of benzene and monosubstituted benzenes; this enabled him to postulate that the π-electron system of benzene in the σ-complex is perturbed to a much lesser extent than is represented in structure (I) and that the benzene carbonium ion has the structure (II), in which the added proton is held by a σ-bond, formed by the electrons located in the *p*-orbital of the carbon atom. Such a structure can then be regarded as a "localised" π-complex differing from the usual π-complexes in which identical interactions of the proton with all the π-electrons of the aromatic sextet are assumed.

In the infrared spectra of complexes of methylbenzenes with $AlBr_3$ and HBr, an intense band has been observed[117] in the vicinity of 2800 cm^{-1}, the band being absent from the spectrum of the complex of hexamethylbenzene; it was assigned to the stretching vibrations of the CH_2 group. The absorption band corresponding to this group is broadened and displaced towards lower frequencies on passing from the anthracene complex to mesitylene, toluene, and benzene complexes, i.e. with decrease in the basicity of the hydrocarbon involved in the formation of the complex.[118] The integral intensity of the absorption bands of the quasi-aliphatic CH_2 groups of the arenium ions increases consistently with increase in their proton-donating capacity (with decrease of the basicity of the hydrocarbon). The less basic the hydrocarbon, the more marked the "acid" character of the hydrogen atoms of the quasi-aliphatic CH_2 group of the arenium ion and the greater its tendency towards involvement in the formation of hydrogen bonds. This leads to a broadening of the absorption band of the CH_2 group, to an increase in its intensity, and to its hypsochromic shift. The authors[118] regard the results as experimental confirmation of the hyperconjugation of the C–H bonds of the quasi-aliphatic CH_2 group with the positively charged carbon atoms of the pentadienyl component of the arenium ions.

This conclusion agrees with the results of a study of the Raman spectra of the mesitylene ion,[119] for which a single absorption band of moderate intensity has been observed in the range 1500–1600 cm^{-1} at 1625 cm^{-1} with a depolarisation coefficient $\rho = 0.65$. A single band of moderate intensity has also been observed in the Raman spectra of mesitylene at 1610 cm^{-1} with $\rho = 0.72$. In the spectra of unsaturated cyclic compounds containing conjugated carbon–carbon bonds of the non-aromatic type,[119] two lines are usually observed, one of which (corresponding to a symmetrical stretch) is very intense and polarised ($\rho = 0.1$–0.2). For aromatic compounds of the benzene series, the corresponding lines are depolarised ($\rho = 0.7$–0.8).[119] The position, degree of depolarisation, and relative intensity of the line of the mesitylene ion are evidence that the formation of the CH_2 group on protonation of mesitylene does not induce a complete overlap of the conjugation in the ring. This is possible only in the presence of an intense hyperconjugation of the C–H bonds in the CH_2 group with the pentadienyl component of the ion. The hypsochromic shift of certain vibration frequencies in the spectrum of the arenium cation $C_6H_7^+$ [113] (Table 9) relative to the frequencies of the analogous vibrations of the $C_6H_7^\cdot$ radical[112] must be attributed to an increase in the corresponding force constants.

Pellois et al.[120] investigated the quasi-line fluorescence spectrum of the triphenylmethyl radical $Ph_3C^\cdot$ obtained as a result of the photodissociation of triphenylmethane at 9 K in a methylcyclopentane matrix. The spectrum is due to the 0–0 transition and consists of ~50 bands in the region of 19 400 cm^{-1}. The spectrum was interpreted on the assumption that the triphenylmethyl radical should be assigned to the D_3 symmetry point group (on the basis of the data obtained with the aid of electron diffraction).

Weston et al.[121] investigated the infrared spectra and assigned the vibration frequencies of the triphenylmethyl cation $Ph_3C^+_{(1)}$ and its isotope-substituted analogues (with 1-^{13}C and Ph-d_5). It was concluded that the cation belongs to the D_3 symmetry point group, in agreement with the X-ray diffraction data, according to which the three central C–C bonds lie in a single plane. The length of each is 1.45 ± 0.018 Å, which is much less than the length of a single C–C bond (1.54 Å). The aromatic rings are slightly non-planar and are displaced from the plane of the C–C bonds by 32° in a propellar fashion. The lengths of the C–C bond within the limits of the rings [1.41, 1.36, and 1.37 Å for C(1)–C(2), C(2)–C(3), and C(3)–C(4) respectively] differ somewhat from that in benzene (1.40 Å). Comparison of the frequencies in the spectra of the triphenylmethyl radical and the triphenylmethyl cation indicates an appreciable increase of the Ph–C vibration frequency (from 1300 cm^{-1} for the radical to 1395 cm^{-1} for the cation), in agreement with the decrease of the Ph–C bond length in the case of the cation. The increase in out-of-plane deformation vibration frequencies of the C–H bonds in the ring corresponds to a decrease of the π-electronic charges on the carbon atoms. The decrease (by 15 cm^{-1}) of the stretching vibration frequency of the bonds in the ring and the increase (by 15 cm^{-1}) of the in-plane C–H deformation vibration frequencies are apparently caused by a change in the force constants of the ring bonds as a consequence of the change in their lengths.

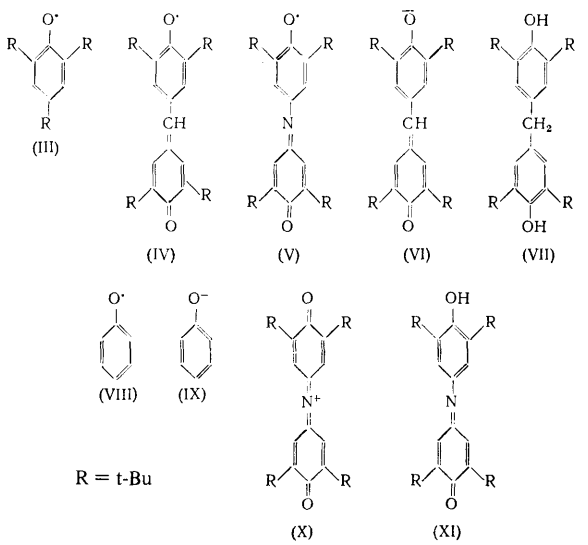
Meda et al.[122] investigated the resonance Raman spectra of the triphenylmethyl cation and anion on excitation by an argon laser. Their vibration frequencies differ very little, since the two electrons of the anions are located in a non-bonding molecular orbital. Appreciable differences are observed between the intensities and particularly between the degrees of depolarisation of the principal polarised bands. It has been suggested that the cation has the D_3 symmetry (planar propeller), while the anion has the C_3 symmetry (dome-shaped propeller).

The infrared spectrum of the allyl radical[123] consists of 16 bands; the observed frequencies agree in broad outline with the spectrum predicted for the allyl ligand (C_S symmetry) on the basis of data for π-allyl organometallic compounds.[124] However, the number and positions of the bands of the allyl radical in the range 500–1000 cm^{-1} correspond to a higher symmetry (C_{2v}) of this species, for which there are two A_2 type vibrations which are inactive in the infrared spectrum.

Saurissean et al.[125] compared the vibrational characteristics and the structures of the allyl radical $C_3H_5^\cdot$ and the allyl anion $C_3H_5^-$ involved in π- and anionic bonds with metals. The bands due to the skeletal stretching vibrations at 1383 and 1023 cm^{-1} in the infrared spectra of the π-allyl complexes have been interpreted as due to the asymmetric [ν_{asym}(CCC)] and symmetrical [ν_{sym}(CCC)] vibrations. The bands at 1491 and 1232 cm^{-1} have been assigned to the same vibrations on the basis of a theoretical analysis of the molecular vibrations.[124] In the case of ionic compounds, the bands at 1527 and 1022 cm^{-1} correspond to the ν_{asym}(CCC) and

ν_{sym}(CCC) vibrations. Calculations have shown that, on passing from $C_3H_5^{\cdot}$ to $C_3H_5^-$, there is a small increase of the force constants K_{C-C} and also an increase of the CCC angle from 120° to 140°. The observed decrease of the frequencies of the in-plane deformation vibrations of the CH_2 and CH groups (from 5 to 8%) reflects the change in the corresponding force constants. The intensities of the in-plane vibration bands of the CH_2 group increase on passing from the π-complexes to the ions, while the opposite behaviour has been observed for the out-of-plane deformation vibrations of the same groups. This indicates a strong anisotropic perturbation of the π orbitals in $C_3H_5^-$. The half-widths of the majority of the intense bands in the spectra of ionic compounds are much greater in the spectra of the π-complexes.[125] Thus the band half-width for the vibrations of the CH_2 group changes from 10 to 50 cm^{-1} and that for δ(CCC) changes from 15 to 75 cm^{-1}. This change is caused by the greater localisation of the electrons at the CH_2 groups in the anion as compared with the radical. The vibration frequencies of the C–H bonds in the π-complexes, which are in the range above 3000 cm^{-1}, are consistent with the aromatic character of these bonds. The ν(C–H) frequencies for the ions are observed at 2990 cm^{-1}.

The infrared spectra of the sterically hindered phenoxy-radicals (III)–(V) have been studied systematically.[126,127] The Raman spectrum of the radical (IV) has also been investigated;[128] the frequency assignment is identical with that carried out by Samoilenko and Kotorlenko.[127]

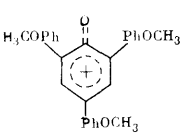


The spontaneous Raman spectra of the phenoxy-radical $C_6H_5O^{\cdot}$ [129] have five polarised bands in the frequency range below 1700 cm^{-1}: at 1615, 1596, 1485, 1382, and 1202 cm^{-1}. The first has been assigned to the vibrations of the C–O$^{\cdot}$ bond, which agrees with other data.[126] The results of Shindo and Hiraishi[129] confirm the conclusion that there is a significant difference between the vibration frequencies of the phenoxy-radical and the corresponding phenol, which had been reached earlier[126,127] on the basis of the change in the force field parameters and not the mode of the vibrations.

The intense band at 1613 cm^{-1} in the resonance Raman spectrum of the radical (IV) has been attributed[130] to the stretching vibration on the C–O$^{\cdot}$ bond, in agreement with the earlier assignment.[127,128] The intense Raman band at 1585 cm^{-1} and the weak band at 1560 cm^{-1} were assigned[130] to the ν_{8a} and ν_{8b} vibrations respectively, while the weak bands at 1540 and 1528 cm^{-1} were assigned to the ν_{19a} and ν_{19b} vibrations.

It is impossible to agree fully with this interpretation, because, owing to the presence in the radical of two equivalent rings, each vibration is split into two. Taking into account the results of the calculation of the vibration spectrum of the radical (IV),[127] the two bands at 1585 and 1560 cm^{-1} must be attributed to the ν_{8a} vibration, which is split into A_1 and $B_1(C_2)$, while the bands at 1540 and 1528 cm^{-1} must be assigned to the ν_{19b} vibration also split into A_1 and B_1 respectively. The band at 1336 cm^{-1} should apparently be assigned to the symmetrical vibration of the bridge and that at 1292 cm^{-1} to the ν_{19a} vibration. The bands at 1226 and 1212 cm^{-1} can be interpreted as due to the ν_{18a} and ν_{18b} vibrations. This interpretation corresponds to the calculated frequencies[127] and agrees with experimental data. For the excited state, the C–O$^{\cdot}$ vibration frequency falls to 1543 cm^{-1} as a result of the interaction with the system of π-bonds. It has been concluded that the resonance Raman spectra can be recorded at concentrations of this radical less than 10^{-7} M, which makes this method promising for the investigation of radical reactions in experiments involving pulse radiolysis.

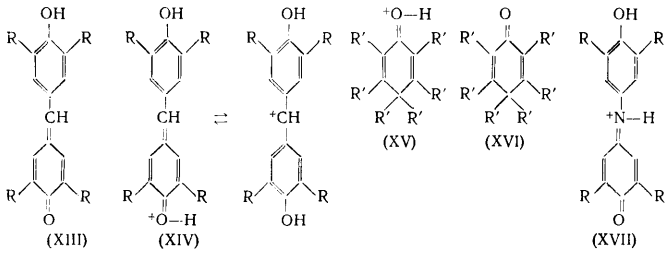
On the basis of infrared, Raman, and electronic absorption spectra, Aleksandrova and Kotorlenko[128] concluded that the rings of the anion (VI) are equivalent, as a consequence of which its symmetry (C_2) is analogous to the local symmetry of the molecule of the phenol (VII) and the radical (IV). Comparison of the vibrational spectra of the anion (VI) with those of the phenol (VII) and the radical (IV) led the authors[128] to the conclusion that the vibration frequencies of the anion have intermediate values between those of the phenol and the radical and that they are closer to the frequencies of the phenol. The hypsochromic shift of the vibration band of the C–O$^-$ bond in the phenoxide anion (VI) relative to the phenol (VII) (by 40 cm^{-1}; Table 10) is close to that obtained[131] for the unsubstituted anion (VIII) and the corresponding phenol (IX) (25 cm^{-1}). The calculated change in the force constant of the C–O$^-$ bond of the anion (VI) compared with the constant for the phenol (VII) is 0.36×10^{-6} cm^{-2}, while for the radical (IV) it amounts to 6.88×10^{-6} cm^{-2}. The slight increase of the vibration frequency of the C–O$^-$ bond and of the force constant K_{C-O} in the spectrum of the anion (VI) compared with the phenol (VII) enabled the authors to assume that the negative charge of the anion is localised predominantly on the two oxygen atoms and that this is responsible for the similarity of the spectra of the anion (VI) and the phenol (VII). The intense band at 1625 cm^{-1} was assigned to the C–O bond of the cation (X),[132] because, according to quantum-chemical calculations, it should be located between ν(C–O$^{\cdot}$) for the radical (V) (1586 cm^{-1}) and ν(C=O) for the indophenol (XI) (1642 cm^{-1}). The assignment agrees with the presence in the infrared spectrum of the cation (XII) of the ν(C⋯O) band at 1613 cm^{-1},[133] and is confirmed by the presence in the infrared spectrum of the cation (X) of a band at 1865 cm^{-1}, which has been interpreted[132] as being due to the asymmetric stretching vibration of the conjugated bond system C=N=C.



(XII)

The bathochromic shift of this band relative to the band of the ion NO_2^+ (2360 cm^{-1}) can be explained by the greater shift of the electron density to N^+ from the C=N bonds than from the N=O bonds. The increase of the force constant of the C=O bond in the cation (X) compared with that of the

radical (V) is 0.78×10^{-6} cm^{-2}. The formation of the cation (XIV) in the interaction of the phenol (XIII) with acids has been demonstrated.



(XIII) (XIV) (XV) (XVI) (XVII)

R = t-Bu, R′ = Me

The similarity of the infrared spectrum of the latter cation to that of the anion (VI) as regards the number and positions of the bands enabled the authors[132] to conclude that these molecules belong to the same symmetry group (C_2). This means that the cation (XIV) has two equivalent rings and two OH groups, which has been confirmed by ^{1}H NMR spectra.

The absorption by the hydroxy-group is observed in the infrared spectrum of the cation (XIV) in the region of 3570 cm^{-1}. The high frequency of this band is consistent with the ^{1}H NMR data, indicating the localisation of the positive charge predominantly on the carbon atom of the bridging CH group. The intense band at 1203 cm^{-1} has been assigned to the vibration of the C–O bond. The shift of the band by 45 cm^{-1} compared with the corresponding band of the phenol (XIII) (1158 cm^{-1}) was explained by the author by the redistribution of electron density. The increase of the force constant of the C–O bond in the cation (XIV) relative to compound (XIII) owing to the increase of the amount of double bond character was 0.64×10^{-6} cm^{-2}.

The formation of the hydroxyhexamethylbenzenium cation (XV) on interaction of hexamethyldienone (XVI) with $AlCl_3$ and HCl in CH_2Cl_2 has been investigated.[134] The broad band at 3450 cm^{-1} has been assigned to the stretching vibration of the OH group involved in the hydrogen bond. The 1510 cm^{-1} band was assigned to the stretching vibration of the C–O bond and the band at 1630 cm^{-1} was assigned to the vibrations of the C–C bonds of the ring with an order of 1.5. It is noteworthy that the shift of the positive charge to the bridging carbon atom induces a rearrangement of the quinonoid ring into an aromatic form, while in the cation (XV) the quinonoid structure is largely retained.

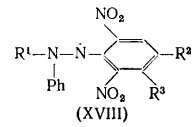
Bands referring to the vibrations of the phenyl and quinone imine rings have been observed[132] in the infrared spectrum of the cation (XVII) obtained by the protonation of the phenol (XI) at the nitrogen atom. A bathochromic shift of the vibration band of the O–H bond at 3615 cm^{-1} relative to the spectrum of compound (XI) (3627 cm^{-1}) has been observed. The broad band at 3515 cm^{-1} was assigned to the $\overset{+}{N}$–H vibration, while the bands at 1640 and 1660 cm^{-1} were assigned respectively to the vibrations of the C=C and C=O bonds of the quinone imine ring. The bathochromic shift of the O–H and N–H bond vibrations relative to the neutral molecules led to the conclusion that the $\overset{+}{N}$–H bond is stronger than the $\overset{+}{O}$–H bond, which was confirmed by chemical experiments. Since the analysis of the vibration modes of phenol, the radical, and the quinonoid structures[126,127] indicates the predominant contribution of the same coordinate to the vibrations in question, the observed frequency shifts and the changes in the force constants permit inferences about the changes in the structures of the compounds in the series under consideration (Table 10).

It follows from the analysis of the data in Table 10 that the addition of a proton to the carbonyl group of the phenol and of an electron to the radical diminishes while the abstraction of an electron and the addition of a proton to the nitrogen atom of the bridging group increases the contribution of quinonoid structures.

Table 10. The vibration frequencies and force constants of the bonds in phenols and the corresponding radicals and ions.

Species	ν (C–O), cm^{-1}	ν (CO), cm^{-1}	ν (C=O), cm^{-1}	$10^6 K_{C-O}$, cm^{-2}	$10^6 K_{CO}$, cm^{-2}	$10^6 K_{C=O}$, cm^{-2}	Refs.
(IX)	1256	—	—	—	—	—	[131]
(VIII)	1281	—	—	—	—	—	[131]
(XV)	—	1510	—	—	—	—	[134]
(III)	—	1573	—	—	—	—	[132]
(XVI)	—	—	1635	—	—	—	[134]
(XIII)	1158	—	1615	7.00	—	14.90	[132]
(VI)	1195	—	—	7.36	—	—	[128]
(XIV)	1203	—	—	7.64	—	—	[132]
(IV)	—	1583	—	—	13.88	—	[127]
(XI)	1156	—	1642	—	—	—	[127]
(XVII)	1203	—	1660	—	—	—	[132]
(V)	—	1586	—	—	—	—	[137]
(X)	—	—	1625	—	—	—	[132]

The infrared spectra of a series of free radicals of the hydrazine type (XVIII) have been investigated:[135,136]



(XVIII)

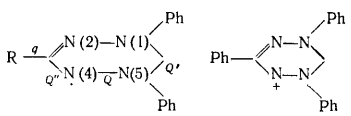
It has been noted that the intense doublet in the spectrum of the radical (XVIII) (bands at 1620 and 1600 cm^{-1}), assigned to the skeletal vibrations of the picryl and monosubstituted rings respectively, has undergone a bathochromic shift by ~20 cm^{-1} compared with the initial molecule, which is due to the increased conjugation owing to the appearance of an unpaired electron at the β-nitrogen atom. The moderately intense band in the range 1210–1250 cm^{-1} has been assigned to the stretching vibrations of the central N–N fragment. On excitation of the diphenylpicrylhydrazyl radical (DPPH) in benzene by means of a pulsed tunable dye laser (λ = 4880 Å), Wilbrandt et al.[137] observed an increase of the intensity of this band in the resonance Raman spectrum.

The spontaneous Raman spectra of the DPPH radical and of the initial diphenylpicrylhydrazine were obtained in a later study.[138] It was noted that, on passing to the radical, the analogous bands undergo a bathochromic shift, because the unpaired electron occupies as a rule antibonding molecular orbitals. New bands at 1205 and 1292 cm^{-1}, having moderate and low intensities respectively, have been observed in the spectrum of the DPPH radical. The authors[138] suggest that the bands at 1280 and 1290 cm^{-1} in the spectra of the molecule and the radical can be analogues, but noted that the increase of the frequency of this vibration on passing from the hydrazine molecule to the radical is then obscure and requires interpretation. The authors[138] proposed such an interpretation of the bands on the grounds that the vibrations of the >N–N–C< group in both species are quasi-characteristic. In the hydrazine molecules this

chain should be bent and a single intense fully symmetrical vibration should appear accordingly in the spontaneous Raman spectrum. In solutions of the DPPH radical the above chain straightens out, which is accompanied by a change in the hybridisation of the bonding orbitals of the N atom from sp^2 to sp. This leads to additional and significant asymmetry owing to the delocalisation of the unpaired electron. In conformity with selection rules, two fully symmetrical stretching vibrations now become active in the spontaneous Raman spectrum, to which the authors[138] assigned new bands at 1205 and 1292 cm^{-1}. Both these vibrations should be intense also in the infrared spectrum, which has indeed been observed.[136] The observed change in the geometry of the species rules out the possibility of comparing the N–N bond vibrations in the diphenylpicrylhydrazine–DPPH radical pair in solutions. According to the above data,[138] when the DPPH radical passes to a crystalline state, the hybridisation of the orbitals of the nitrogen atom again changes from sp (for the solution) to sp^2 and coincides with that for the initial molecule.

Mielke and Ratajczak[139] carried out a calculation for the normal vibrations of the molecule of hydrazine and its protonated derivatives $N_2H_5^+$ and $N_2H_6^{2+}$ in terms of a modified valence force field approximation. It was found that the diagonal force coefficients, ν(N–N), and δ(HNH) decrease monotonically on passing from N_2H_4 to $N_2H_6^{2+}$. The observed distribution of the potential energy indicates the absence of a significant change in the vibration modes for $N_2H_6^{2+}$. This finding suggests that the decrease of the force constant for the N–N bond on passing from hydrazine to protonated hydrazine is due to the decrease of the degree of delocalisation of the unshared electron pair from the nitrogen atoms to the N–N bond.

Studies of the infrared spectra of stable verdazyl radicals (XIX) have been considered in reviews:[1,140]



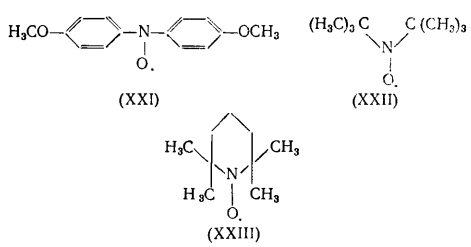
(XIX) (XX)

R = Ph (TPV), H

However, the assignment of the frequencies to the vibrations of individual bonds was not rigorous, since the similarity of the atomic weights of nitrogen and carbon entails an intense interaction and the normal vibrations of the heterocycle must have complex modes. For a reliable interpretation of the spectrum of the triphenylverdazyl radical (TPV) (XIX), a calculation has been made[141] of the frequencies and modes of the vibrations for two conformations—chair and boat. The correctness of the force field parameters obtained has been confirmed by the satisfactory agreement between the calculated and experimental changes in the vibration frequencies of the heterocycle with the ^{15}N atoms in the 2- and 4-positions. The calculation showed that the vibrations of the heterocycle of the TPV radical are described by complex modes. The interpretation of the complex band at 1330 cm^{-1} was revised and it was shown that it consists of two bands, the more intense of which (at 1330 cm^{-1}) is caused mainly by the deformation of the angles β(NCH), while the band at 1315 cm^{-1} is due to the vibrations of the N–Ph bonds. In addition the bands at 1400 cm^{-1} [Q''(CN), Q'(C–N)] and at 1380 cm^{-1} [q(C–C), Q(N–N), Q''(CN)] were assigned to the vibrations of the heterocycle.

The change in the infrared spectra on one-electron oxidation of the TPV radical to the corresponding cation (XX) has been investigated.[141,143] In order to obtain a quantitative characteristic of the change in the electronic structure following the abstraction of an electron from the TPV radical, the vibrational spectrum of the cation (XX) having the boat conformation was carried out. The geometrical structure of this cation was found quantum-chemically by minimising the total energy of the corresponding system with respect to the nuclear coordinates; it was shown that it differs insignificantly from the geometrical structure of the TPV radical. The experimental[141] band shift on passing from the TPV radical to the cation (XX) made it possible to find the changes in the bond force constants and the interaction constants. The increase of the force constant K_Q corresponds to a shift of electron density from the nitrogen atoms in the 1- and 5-positions to the N–N bonds, which agrees with the abstraction of an electron from the nitrogen atoms in the 2- and 4-positions on oxidation of the TPV radical to the cation (XX), which has been established on the basis of quantum-chemical calculations and X-ray electronic spectra.[144] The decrease of the force constants K_Q and K_q indicates an increase of the positive charge on the N(1) and N(5) atoms, while the decrease of the interaction constants $H_{QQ''}$, $H_{Q''Q''}$, and H_{Qq} agrees with the decrease of the degree of delocalisation of the unshared electron pair from the N(1) and N(5) atoms to the benzene rings, as a consequence of which the frequency of the out-of-plane deformation vibrations of the hydrogen atoms in the benzene rings increases and the intensity of their stretching vibrations diminishes.

The band at 1345 cm^{-1} in the spectrum of the dimethoxydiphenylnitroxy-radical (XXI) has been assigned to the vibration of the N–O$^{\cdot}$ bond.[135] Comparison of the infrared spectra of the di-t-butylnitroxy-radical (XXII) [145] and the 2,2',6,6'-tetramethylpiperidin-1-yloxy-radical (XXIII) [146] with the infrared spectra of the corresponding amines established that the N–O$^{\cdot}$ band is also at 1345 cm^{-1}.

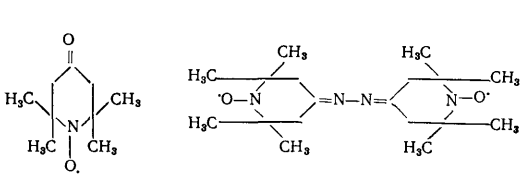


(XXI) (XXII)

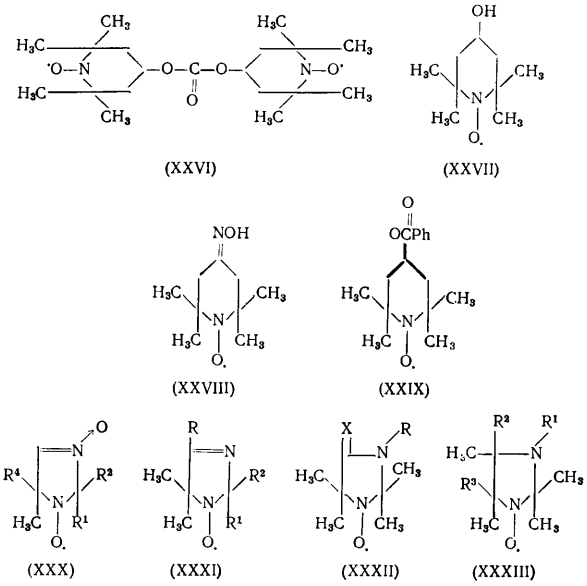
(XXIII)

The similarity of the atomic weights of carbon, nitrogen, and oxygen raises the question of the extent to which the vibrations of the N–O$^{\cdot}$ bond are characteristic. A study has been made[147] of the infrared spectra of the radicals (XXII) and (XXIII) and also the frequencies and modes of their normal vibrations were calculated, which served as a basis for the interpretation of their vibration spectra, a model was proposed for the force field, and it was shown that the vibrations of the N–O$^{\cdot}$ bond are characteristic as regards frequency, mode, and intensity.

It has been shown with the aid of the ^{15}N label[148] that the N–O$^{\cdot}$ band in the infrared spectra of other radicals of the piperidine series is at 1380 cm^{-1} [the radicals (XXIV) and (XXV), 1367 cm^{-1} [the radical (XXVI)], and 1371 and 1342 cm^{-1} [the radical (XXVII)].

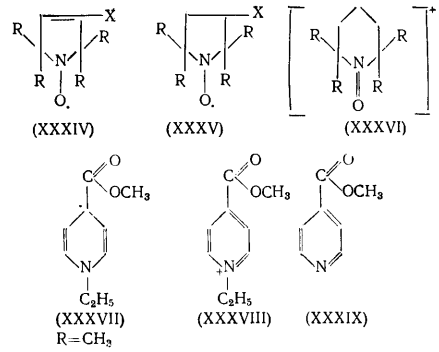


(XXIV) (XXV)



Intense bands, assigned to the vibration of the N—O bond, have been observed in the Raman spectra of the radicals (XXIV) and (XXVII) [149]—at 1370 cm^{-1} for (XXIV), at 1370 and 1359 cm^{-1} for (XXVII), and at 1362 and 1352 cm^{-1} for the radicals (XXVIII) and (XXIX) respectively. The higher N—O· bond vibration frequency for the radical (XXIV) compared with (XXIII) can be accounted for by a difference in its steric structure. While the radical (XXIII) has the chair conformation,[150] the radical (XXIV) has the twisted boat conformation with an angle of twist at 28°.[151] The increased order of the exocyclic bond in the 4-position promotes the delocalisation of electrons in the ring,[152] which is accompanied by an increased amount of double bond character of the N—O· bond and an increase in the corresponding frequency. The presence of two bands in the spectrum of the radical (XXVII) is apparently caused by both intramolecular and intermolecular hydrogen bonds. In dilute solutions this radical has the boat conformation with an intramolecular hydrogen bond,[151] whereas in the crystalline state the molecules are linked by hydrogen bonds into infinite chains and have a distorted chair conformation.[151] The similarity of the N—O· bond vibration frequencies in the spectra of the radicals (XIX) and (XXIII) agrees with the conclusion of Kotorlenko et al.[147] that there is no shift of the N—O· bond vibration frequency when the hydrogen is replaced by carbon at the C(3) atom of the radical (XXIII) and also that the vibration mode remains unaltered.

The N—O· bond vibration frequencies for radicals of the imidazoline [the radicals (XXX) and (XXXI)] and imidazolidine [the radicals (XXXII) and (XXXIII)] series have been interpreted on the basis of their Raman spectra and also by measuring the isotope shift after the introduction of ^{15}N in the 1-position in the imidazoline ring. It has been established that the vibration band of the N—O· bond in the infrared and Raman spectra of these radicals is at 1438 ± 5 cm^{-1} and the observed isotope shift (27 cm^{-1}) agrees with the calculated value (28 cm^{-1}). Calculation of the frequencies and modes of the normal vibrations of these radicals[149] showed that the vibration of the nitroxy-group is characteristic in terms of the frequency. The N—O· bond vibration bands of five-membered nitroxy-radicals of the pyrroline [the radical (XXXIV)] and pyrrolidine [the radical (XXXV)] series are located in the same part of the spectrum. It has been concluded[149] that the position of the N—O· band in the spectra of cyclic nitroxy-radicals depends on the ring size.



The vibrational spectra of nitroxy-radicals and biradicals in the region of the stretching vibrations of unsaturated carbon—carbon bonds and the stretching vibrations of the CH and OH groups have been investigated by Bovina et al.[153]

The conversion of the nitroxy-radical (XXIII) into the corresponding cation (XXXVI) is accompanied by a change in the N—O· bond vibration frequency from 1345 cm^{-1} for the radical to 1630 cm^{-1} for the cation, which is caused by the decrease of the length of this bond from 1.30 Å [154] to 1.19 Å [152] respectively and in addition by the change from the chair conformation (XXIII) [150] to the twisted boat conformation (XXXVI) with an angle of twist of 24°30′.[152] The decreased length and the strengthening of the N—O· bond following the one-electron oxidation of the radical (XXIII) has been explained[152] by the fact that the unpaired electron in nitroxy-radicals is located in an antibonding orbital and that the conversion of these radicals into cations entails the loss of this electron. In our view, the oxidation of the radical (XXIII) to the cation (XXXVI) is accompanied by the abstraction of an electron from the unshared electron pair of the nitrogen atom with subsequent pairing of the two unpaired electrons located in the O and N atoms.

Kosover and Poziomek[155] quote the C=O bond vibration frequencies for 1-ethyl-4-methoxycarbonylpyridinium iodide (XXXVIII) (1730 cm^{-1}), 1-ethyl-4-methoxycarbonylpyridinyl (1642 cm^{-1}) (XXXVII), and methyl isonicotinate (XXXIX) (1736 cm^{-1}), which increase the decreased degree of displacement of the electron density to the ring. On the other hand, the ring stretching vibration frequencies diminish on passing from the pyridinyl radical (XXXVII) [156] to protonated pyridine[157] and further to pyridine (XXXIX).[109]

Thus the abstraction of an electron from neutral polyatomic free radicals is accompanied, as in the case of the simple radicals, by an increase of the vibration frequency and strength of the bond adjoining the atom from which the electron is abstracted, while the addition of an electron entails a decrease in the vibration frequency and order of the bond.

Comparative analysis of the vibrational spectra of neutral free radicals and the corresponding ions—the products of the one-electron reduction or oxidation of these radicals—makes it possible to infer the changes in both the geometrical and electronic structures of the species and to predict the sites of increased reactivity.

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