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Vibrational Spectra of Free Radicals

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A survey of results obtained on the vibrational spectra of simple free radicals, polyatomic neutral radicals, and polyatomic radical-ions is accompanied by 141 references.

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I. INTRODUCTION

The vigorous development of the chemistry and physics of free radicals during recent years is due to their important role as intermediate species in many chemical reactions and biological processes. Simple free radicals have been detected in the spectra of planets, comets, and stellar objects. Many problems of structural and theoretical chemistry, as well as chemical kinetics, are solved by means of free radicals. Such questions as the structure of electron shells and their modification under the influence of perturbations, the mechanisms of chemical reactions and physical processes causing magnetic relaxation of nuclei, etc. can be settled. Interest in free radicals arises also from their widespread application in many fields of science and technology. They are used as paramagnetic probes and spin labels in the physical chemistry of polymers, biophysics, and molecular biology. Stable free radicals act as inhibitors of the degradation of polymeric materials in technology. Many of them are employed in magnetometers and radio-frequency lasers.

Detailed studies have been made of the chemical properties, electron spin resonance spectra, and electronic spectra of free radicals, and their electronic structure has been calculated by quantum-chemical methods. The Nobel Prize was awarded in 1971 for a long series of investigations on the electronic spectra of simple radicals (Herzberg's monograph[1]). However, little work has been done on the vibrational spectra, which give valuable information both for identifying free radicals and for determining their electronic structure. The vibrational spectra of simple radicals have been more fully studied. Two reviews[2,3] have covered the literature on their infrared spectra up to 1971. The data given in most papers on the vibrational spectra of polyatomic radicals are fragmentary and non-systematic. Only quite recently have the first publications appeared in which the problem of interpreting vibrational spectra for several neutral and charged polyatomic radicals has been posed and more or less solved, and their force field has been estimated.

The present Review examines the literature on the vibrational spectra of neutral and charged polyatomic free radicals, as well as recent publications on the spectra of simple radicals not covered in the 1971 reviews by Andrews and by Milligan on the infrared spectra of simple radicals stabilised in neutral rigid matrices. Papers on the spectra of polyatomic radical-ions have been divided into three groups. The first comprises those with qualitative descriptions of spectra and an approximate assignment of one of two bands. The second group combines investigations on the variation of several characteristic frequencies in series of radical-ions of similar structure. The third group consists of recent papers giving an interpretation of the vibrational spectra of several stable radical-ions based on the calculation of normal vibrations, as well as an estimate of their force field and a comparison of the force constants with parameters of their electronic structure.

II. VIBRATIONAL SPECTRA OF SIMPLE FREE RADICALS

Simple free radicals comprising a few atoms are very unstable owing to their very great chemical activity, so that the recording of their vibrational spectra presents considerable difficulties. Since their lifetime is very short (10^{-3}–10^{-5} s), two approaches have been made to determining the vibrational spectra of such radicals: (1) the free radicals were fixed in rigid, inert matrices, which lowered their reactivity and lengthened their lifetime to such an extent that the usual instruments could be used; or (2) an infrared spectrometer having a scanning time < 1 ms was used. Since the production of such an instrument is a complex technical task, accomplished not long ago[4,5], the matrix isolation of free radicals has become widely used. The possibility of thereby obtaining infrared spectra of free radicals, as well as unstable molecules and ions, was demonstrated by Pimentel and his coworkers, and this method was developed and perfected in his own laboratory. Details of the method of matrix isolation have been given in the reviews[2,3], together with a discussion of procedures for obtaining simple radicals and identifying them from their spectra. In almost all the above studies the reliability of the assignment was improved by investigating every possible isotopic variety of the radicals and comparing the spectra of radicals prepared in different ways.

The reviews give results on the infrared spectra of methyl and halogenomethyl radicals, as well as radicals obtained by adding a third atom to a diatomic molecule (e.g. HCO, HalCO, HalOO, HOO), halogenated radicals (e.g. OF, OCl, CF, CCl, NF_2), radicals obtained by the photolysis of silane and halogenated silanes, and several others. Much of the work covered in the reviews was in a stage of further development, as is indicated by the appearance of communications on continued investigations of the infrared spectra of the radicals mentioned[2,3]. Thus a higher concentration of the HO_2 radical has been obtained[6] than in previous work. The spectra of four compounds of

formula DO_2 differing in isotopic composition with respect to oxygen have been reported for the first time. Calculation of the vibrations of HO_2 having various isotopic compositions confirmed the previous assignment of the 1389-cm^{-1} band to the deformation vibration of OOH, but the 1101-cm^{-1} band to the O–O stretching vibration. A bond angle of 105 ± 5° gave good agreement with experiment for DO_2. The relatively low force constant of the O–H bond in HO_2 and the near equality of the force constants of the O–O bonds in HO_2 and O_2 are compatible with the close similarity of their electronic structures, evident in the location of the corresponding electron transitions in the same spectral range. A recent analysis[7] of the vibrational spectra of peroxyl and deuteroperoxyl obtained in various ways reveals a positive isotopic shift of the ν_3 vibration (1101 and 1123 cm^{-1} for HO_2 and DO_2 respectively) and a negative shift for ν_2 (1389 and 1020 cm^{-1}). Analysis of the spectral data for isotopically substituted derivatives of the HO_2 radical led to the conclusion that the oxygen atoms were not equivalent, which showed that the radical has an unsymmetrical structure.

The frequency of the out-of-plane deformation vibration of the methyl radical (611 cm^{-1}) differs significantly from the harmonic approximation. Riveros showed[9] that this discrepancy is consistent with the planar structure of the radical established from electron spin resonance data if the anharmonicity of the out-of-plane motion is taken into account. This success led Smith and Andrews[10] to use perturbation theory to calculate the anharmonic potential function of the ground state for out-of-plane deformations in the series of radicals CH_2X (where X = Cl, Br, I). The calculated potentials were compared with the harmonic functions, and employed to confirm the observed isotope shifts. With CH_3 and CH_2X the quartic anharmonic constants make a significant contribution to the potential energy, so that the harmonic force constants are considerably too low. Subsequently these workers extended the range of halogenomethyl radicals studied by infrared spectroscopy, by investigating the tri-,[11] di-,[11] and mono-iodomethyl[12] radicals. The 1106-cm^{-1} band in the spectrum of CHI_2 was assigned to oscillation of the HCI angle, and the 716-cm^{-1} band to an antisymmetric stretching vibration of the C–I bonds. With CDI_2 these vibrations give bands at 850 and 653 cm^{-1} respectively. The 693-cm^{-1} band of the CI_3 radical is attributed to stretching of the C–I bonds. The spectrum and the force field of CH_2I were compared with the corresponding characteristics of the other monohalogenomethyl radicals. All three iodomethyl radicals show an unusually large force constant of the C–I bond in comparison with the value for sp^3-hybridised carbon atoms. It was considered that the change in hybridisation from sp^3 to sp^2 was insufficient to explain this observation, and π-bonding of the $\pi(p-p)$ and $\pi(p-d)$ type was assumed.

Milligan and his coworkers[13] examined the infrared spectra of the two halogenated methyl radicals $CClF_2$ and CCl_2F, and established that, as in $CHCl_2$ and CCl_3, the carbon–chlorine bond in CCl_2F is considerably stronger than in stable molecules. Considering the possibility that the bond is strengthened by the presence of $\pi(p-d)$ interaction, these workers point out that such interaction will be considerable with a planar or almost planar structure, but a non-planar structure has been established for trichloromethyl.

One of the few studies demonstrating the possibility of applying yet another method of vibrational spectroscopy to unstable free radicals is an investigation of the Raman spectrum of the OF radical obtained photolytically on exposure in an argon matrix to a laser source[14]. The results support the assignment based on the infrared spectrum.

Investigation of the Raman spectra of the NF_2 radical in the gaseous state at high temperatures (up to 250°C)[15] is equally interesting from the point of view of technique. The frequencies of the completely symmetrical vibrations ν_1 = 1074 cm^{-1} and ν_2 = 572 cm^{-1} agree well with the corresponding frequencies in the infrared spectrum of the gaseous state.

The frequencies of the free radical NCN observed in the infrared spectrum in different matrices have been given[16–18] as ν_2 = 423 cm^{-1} and ν_3 = 1475 cm^{-1}. The 2672-cm^{-1} band detected at high concentrations of the radical was interpreted[19] as $\nu_1 + \nu_3$, which yielded ν_1 = 1197 cm^{-1}.

The spectrum of the CNN radical in a matrix contains the bands[20] ν_2 = 393 cm^{-1}, ν_1 = 1241 cm^{-1}, and ν_3 = 2847 cm^{-1}. From the estimated force constants it was concluded that the CN bond was almost triple, and the NN bond almost double. Vibration frequencies of the diazomethyl radical HCNN and its deuterated analogue were given[21] without interpretation. The bands at 1756, 1158, and 392 cm^{-1} were attributed[22] to the dicyanomethylene free radical C_3N_2. These wave-numbers are close to those calculated for a linear molecule having the force constants of molecules of similar structure.

Use of a multiple-pass gas cell to give an optical path of 80 m yielded an infrared band at 1360 cm^{-1}, assigned[23] to an antisymmetric vibration of the symmetrical nitrate free radical NO_3 in the gas phase. The corresponding band of the planar nitrate ion lies at 1315 cm^{-1}.

Milligan and Jacox[24] observed the infrared bands ν_2 = 1499 cm^{-1} and ν_3 = 3220 cm^{-1} for the NH_2 radical, displaced to 1496 and 3215 cm^{-1} respectively for $^{15}NH_2$. A band at 1321 cm^{-1} was detected in the spectrum of NDH, and ND_2 was characterised by a band at 1110 cm^{-1}. Investigating the infrared spectrum of NHF and its isotopic analogues, these workers[25] interpreted the observed two fundamental frequencies as ν_2 = 1432 cm^{-1} and ν_3 = 1000 cm^{-1}.

Ogilvie[26] has recently revised the earlier interpretation[27] of the infrared spectrum of the HNO radical, and has suggested a new assignment of bands after comparing the geometrical parameters of the radical with the frequencies: he attributes the band at 2719 cm^{-1} to N–H vibration, and that at 2043 cm^{-1} to N–D, corresponding to the greater lengths of these bonds.

The infrared emission spectrum of the OH free radical has been determined by Murphy[28] for the fundamental and overtone regions. The fundamental band proved to be weaker than had been expected. The relative probabilities of the transitions were determined from the intensity ratio of fundamental and overtone bands, and hence the dipole moment function $\mu(R)$OH was calculated.

All three fundamental frequencies—ν_1 = 985 cm^{-1}, ν_2 = 496 cm^{-1}, and ν_3 = 1042 cm^{-1}—were observed with the SO_2^- radical-anion stabilised as a charge-transfer complex with caesium and other alkali metals in an argon matrix[29]. The isotopic data indicate that interaction between SO_2^- and Cs^+ is slight, so that all vibrational frequencies of normal and isotopic SO_2^- can be calculated in good agreement with experiment without regard to the influence of the caesium ion. The slight splitting of the principal frequencies suggested that the oxygen atoms were not equivalent. Estimates by these workers indicate an SO_2^- bond angle of ~ 160°, while the SO bond was considerably weaker than in SO_2, owing to the addition of the nineteenth valency electron to an orbital that was bonding for the terminal oxygen atoms and antibonding for the SO bonds.

The infrared spectra of the halogen dihalides have been investigated in a matrix[30-32]. The 696-cm^{-1} band in the spectrum of the free radical HCl_2 has been assigned[30] to the ν_3 vibration; the corresponding band in DCl_2 is at 464 cm^{-1}. Examination of the infrared absorption spectrum of the HBr_2 radical gives[31] $\nu_3 = 727$ cm^{-1} and $\nu_1 = 165$ cm^{-1}, and indicates a linear structure ($D_{\infty h}$ symmetry) as for HCl_2. The spectrum of the radical HI_2, also interpreted[32] on the hypothesis of $D_{\infty h}$ symmetry, gave $\nu_3 = 682$ cm^{-1} and $\nu_1 = 121$ cm^{-1}. The potential functions of all three radicals contain a large quartic term, which governs the anharmonicity of the H–Hal vibrations. Inspection of the force constants indicates that the hydrogen bonds are as strong in the $HHal_2$ radicals as in the $HHal_2^-$ ions. Comparison of the force constants in the series of hydrogen dihalides and the corresponding ion leads to the conclusion that the contribution of the quartic term to the potential function is larger for the radicals than for the ions. In the case of the ions the contribution of the anharmonic term diminishes with increase in size of the halogen atom, a tendency that is even more marked in the neutral radicals. Thus removal of an electron from a non-bonding orbital in $HHal_2^-$ has little effect on the hydrogen bond, but a marked effect in increasing the anharmonicity of the potential function. From the results for the above three radicals it was suggested[31] that HF_2 should be stable.

The spectra of the free radicals CO_2^-, CCl_3, and CH_3CO have been recorded[33] in a rotating cryostat enabling infrared and e.s.r. spectra to be determined on the same specimen. Those of the first two radicals were obtained to check the technique; the spectrum of the acetyl radical, obtained for the first time, was investigated in greater detail. The 1796-cm^{-1} band was assigned to a vibration of the carbonyl group; the 958-cm^{-1} band was interpreted as due to a carbon–carbon stretching vibration.

Flash photolysis in the vacuum ultraviolet has recently been used[34] to obtain the radicals C_3, C_3H, C_3H_2, and C_3H_3 isolated in a matrix, as well as the allyl radical, and a preliminary assignment of the infrared bands has been made.

Pimentel et al.[35] obtained the infrared spectrum of the methyl radical in the gaseous state for the range of out-of-plane vibrations (450–740 cm^{-1}), using their method of rapid scanning spectroscopy. The observed frequencies (607 and 603 cm^{-1} for CH_3, 561 and 558 cm^{-1} for CH_2D, and 461 cm^{-1} for CD_3) are close to those of the matrix-isolated radical and its deuterated derivatives, and were assigned to out-of-plane deformation vibrations of umbrella type. The lower frequency was due not to inversion of a pyramidal molecule but to a vibrationally excited methyl radical. The potential function of the out-of-plane vibration was calculated on the hypothesis that the radical had a planar structure. The anharmonicity was described by a quartic term, and could not be neglected in the case of CD_3.

In concluding this Section we may note the procedure suggested by Johnston et al.[36] for observing the infrared spectra of free radicals, based on the method of molecular modulation. Intense flash photolysis gives a fairly high concentration of radicals, with which, owing to fast reactions, it is often possible to observe not the species formed initially but their reaction products. The proposed method enables spectra of free radicals to be obtained at the very low concentrations obtainable with moderate light intensities. The photolysing light is switched on and off periodically, which slightly modulates the concentration of the radicals formed and of other intermediate products. The periodic variation in the concentration of unstable compounds, by slightly varying the absorption, modulates the intensity of the transmitted infrared beam. When the spectrum is scanned, the modulated intensity is obtained only within regions characteristic of the radicals or other short-lived products. Measurements of the phase shift during molecular modulation can be used to estimate the lifetime of the radical. Compounds are in general identified from the position and the form of the infrared bands. But when the spectrum is unknown or the bands overlap, the method permits identification of the absorbing substance as initial reactant, intermediate compound, or secondary product from the magnitude of the phase shift.

The radical ClO, formed photolytically from gaseous chlorine and oxygen, was detected in the gas phase from the absorption spectra and the phase shifts found in this work; the frequency 942 cm^{-1} is consistent with the value for the matrix-isolated radical. Analysis of the phase shifts of the infrared absorption led to assignment of the 1127-cm^{-1} band to the HO_2 radical obtained by photolysis of ozone in the presence of hydrogen peroxide (1101 cm^{-1} in the case of matrix isolation). This method, though technically complicated, may give valuable information on short-lived radicals, especially at very low concentrations.

III. VIBRATIONAL SPECTRA OF POLYATOMIC FREE RADICALS

Little use of vibrational spectroscopy has been made in studying neutral radicals obtained by the homolytic cleavage of bonds. Karagonis[37] was one of the first to employ the infrared spectrum to determine the structure of the triphenylmethyl radical. From the number of infrared-active vibrations it was concluded that a planar structure was the most probable. No features of a radical character have been detected[38] in the infrared spectra of several perchlorodi(and tri)phenylmethyl radicals, merely a slight bathochromic shift in the frequency of the benzene ring ~ 1500 cm^{-1}. An analysis of the vibrational structure of the luminescence spectra of three arylmethyl radicals has been given[39] without assignment of the vibrational frequencies.

A series of papers contain data on the infrared spectra of phenoxy-radicals[40-50]. With 2,4,6-tri-t-butylphenoxyl[40,41] the hydroxyl band of the phenol at ~ 2.7 μm disappears, and the band appearing at 6.4 μm is assigned to the ν(C–O*) vibration (where the asterisk denotes the unpaired electron). From the position and number of carbon–oxygen stretching bands[41-45,48] it was concluded whether the phenoxy-radicals were present in monomeric or dimeric form. The same bands were examined in elucidating structure of the 2,2-bis-(3,5-di-t-butyl-4-hydroxyphenyl)propane diradical[47].

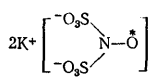
A systematic investigation of the infrared spectra of stable phenoxy-radicals and related molecules has been made[51-53] in order to reveal the influence of the unpaired electron on the force field of the molecule. The infrared spectra of three phenoxy-radicals—2,4,6-tri-t-butylphenoxyl[52], 2,6-di-t-butyl-4-(2,6-di-t-butylquinobenzyl)phenoxyl (galvinoxyl), and 3,3′,5,5′-tetra-t-butylindophenoxyl[53]—have been interpreted. The most significant difference between the spectra of radicals and related molecules (initial phenols and molecules of quinonoid structure) is observed in the region containing carbon–oxygen and cyclic carbon–carbon stretching vibrations. The main

features of the force field of the phenoxy-radicals have been determined, and the changes in the spectra of the radicals in comparison with those of the related molecules were shown to be due mainly to change in the force field, not in the geometrical structure. Analysis of the modes of vibration of phenols, radicals, and quinonoid molecules indicates that the same coordinate makes the predominant contribution to the comparable vibrations. Hence the frequency shifts observed in the phenol–radical–quinonoid sequence are due to change in the force constants, not in the modes of vibration (Table 1). Thus it was suggested[52, 53] that the effect of the unpaired electron on the infrared spectra could be estimated by comparing the force constants of radicals and related molecules. The changes in the frequencies of out-of-plane deformation vibrations of cyclic carbon–hydrogen bonds and in the carbon–oxygen bond intensities for the series of compounds indicate a decrease in the π-electron densities on the carbon atoms forming carbon–hydrogen bonds and also an increase in polarity of the CO bond.

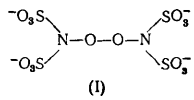
Table 1. Force constants (10^6 cm^{-2}) of ring carbon–carbon bonds and of carbon–oxygen bonds in phenol, the phenoxy-radical, and quinonoid molecules.

Bond	Phenol	Phenoxyl	Cyclohexadienone	Quinone
Q″ q	7,00	13,88	16,02	16,18
Q Q	10,04	11,46	13,95	13,85
Q′ Q′	10,04	8,66	7,85	7,85
Q″ Q″	10,04	9,76	6,77	7,85

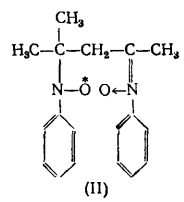
Infrared spectroscopy has been used to elucidate the structure of several nitroxide radicals[3, 54–61]. In the case of Frémy's salt



frequencies have been tentatively assigned to group vibrations for both monomeric and dimeric forms[54, 55]: the stretching frequency of the N–O* bond was assigned to the frequencies 1620 and 1260 cm^{-1} in the two forms. Analysis of the infrared spectrum led to choice of (I) for the structure of the dimer.



(I)



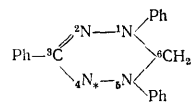
(II)

From an investigation of the infrared spectra of Benfield's radical (II), its derivatives substituted in an aromatic ring, and the initial compounds, Tüdos et al.[56] concluded that the main difference between the spectra of radicals and initial compounds is disappearance of the hydroxyl band at ~ 3300 cm^{-1}. They detected no other spectral features characteristic of radicals.

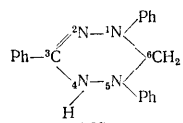
Piperidine nitroxide free radicals were also characterised by their infrared spectra[57–60]. The range 1300–1400 cm^{-1} was studied[58] with the aim of detecting the ^{14}N–O* bond, whose stretching frequency is 1373 ± 7 cm^{-1}.[60] The vibration frequency of the ^{15}N–O* bond was also determined[60], as ~ 1353 cm^{-1}.

The band at 7.43 μm in the spectrum of the dimethoxydiphenylnitroxide free radical was assigned[61] to ν(N–O*). The estimated force constant of this bond (8 mdyn Å^{-1}) is intermediate between the values for single and double bonds.

Several workers[62–64] have used infrared spectroscopy to study the verdazyls, a new class of uncharged stable radicals prepared not long ago. Kuhn and Trischmann[62] assigned the vibrations of the benzene rings in 1,3,5-triphenylverdazyl (III) and in 1,5-diphenylverdazyl, but the vibrations of the heterocycle remained almost unassigned. Qualitative examination of the infrared spectrum suggested that the radical was more symmetrical than the original leuco-base (IV), and the N–H stretching band near 3400 cm^{-1} had disappeared. A fairly complete assignment of the infrared spectra of the verdazyl (III) and its derivatives substituted in one aryl ring was based[63] on the analogy with formazans investigated previously. The 1340-cm^{-1} band was attributed to an NN-stretching vibration in the heterocycle. Other workers[64] assign an intense band at 1145 cm^{-1} to this vibration in the verdazyl (III), and the 1340-cm^{-1} band to a CN-stretching vibration in an *N*-phenyl group.



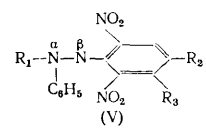
(III)



(IV)

The same paper reports the assignment of the infrared spectra of the initial leuco-base (IV), its analogue deuterated in the heterocycle, and the verdazyl cation (III), and changes in the spectrum accompanying one-electron cation-radical interconversions are traced. The spectra of the leuco-base (IV) and the radical (III) differ significantly in the frequencies of stretching vibrations of the tetrazole ring, whereas the vibration frequencies of the benzene rings remain unchanged. The spectrum undergoes appreciable changes when charged structures are formed from the radical. The frequency of the 1165-cm^{-1} band due to an NN-stretching vibration rises in the spectrum of the cation, whereas that of the 1197-cm^{-1} band due to the $C_{(6)}N$-stretching vibration falls, relative to those of the corresponding vibrations of the radical (1145 and 1208 cm^{-1}); the 1266-cm^{-1} band due to vibration of the $C_{(3)}N$ bond hardly shifts. The vibration frequencies of the phenyl rings undergo little change on formation of the ion. From the frequency shifts of the $C_{(3)}N$- and NN-stretching vibrations for the cation it was assumed[64] that a considerable proportion of the positive charge was localised on the $N_{(1)}$ and $N_{(5)}$ atoms, which is consistent with the quantum-chemical calculation of the π-electron structure of the triphenylverdazyl cation.

Investigation of the infrared spectra of a series of free radicals of hydrazine type having the general formula



(V)

and of the initial hydrazines has revealed[61,65] changes in the spectra due to redistribution of electron density resulting from the appearance of the unpaired electron. The 3300-cm^{-1} band due to NH-stretching vibrations has disappeared from the infrared spectra of stable hydrazyl radicals, and a series of characteristic frequencies are lower than in the original compounds. The strong bands at 1620 and 1600 cm^{-1}, assigned to skeletal vibrations of the picryl residue and of the monosubstituted benzene ring attached to the α-nitrogen atom respectively, have diminished in frequency by 20 cm^{-1}, which is attributed to increasing conjugation resulting from the appearance of the unpaired electron on the β-nitrogen atom. The presence of the unpaired electron explains also the appearance of a new band of medium intensity in the range 1210–1250 cm^{-1}, assigned to stretching vibrations of the central fragment $\rangle N-N^{*}-$.

The infrared spectrum of propene adsorbed on zinc oxide at 125°C shows[66] detachment of a hydrogen atom from the methyl group and the appearance of a band at 1545 cm^{-1}, assigned to vibrations of CC bonds with order 1.5 in the allyl radical. The force constant of this bond was estimated as 7.54 mdyn $Å^{-1}$.

The vibrational spectrum of the benzyl radical, formed by the flash photolysis of toluene or an α-monohalogenated derivative, was obtained by analysing the vibrational structure of the luminescence[67-73] and absorption[74,75] spectra. Emission spectra of the benzyl radical with well resolved vibrational structure were obtained both for the gas phase by means of a long-path cell[69] and for the radical trapped in various matrices at low temperatures[67,68]. The spectra of deuterated analogues of the benzyl radical were also given[70,71], and the vibrational frequencies were interpreted by analogy with toluene. More recently[72] the luminescence and absorption spectra of the benzyl and *o*-, *m*-, and *p*-fluorobenzyl radicals have been obtained in an adamantane matrix, and an analysis was given of the vibrational structure of the spectra of all these radicals. The vibrational frequencies of the benzyl radical agreed well with those obtained earlier. The infrared spectrum of the benzyl radical deposited with a neon matrix on caesium bromide and calcium fluoride windows at the temperature of liquid helium was given[73] without assignment.

The force constants of the benzyl radical were calculated[76] by means of a calibration curve from the bond orders obtained by the Hückel method and also by the self-consistent field method to a semi-empirical approximation allowing for electronic–vibrational interaction[77]. The latter were used[78] in calculating the frequencies and the forms of the normal planar vibrations of the benzyl radical, the equilibrium bond lengths of the radical being obtained by the Pariser–Parr method with variation of the resonance integral β specified as a power function of the bond order. The satisfactory agreement between calculated and observed frequencies permits the hope that quantum-chemical estimation of bond lengths and force constants could be applied to solving the vibrational problem for free radicals. Comparison of the vibrational spectra of isoelectronic radicals—phenoxyl and benzyl—indicates that the force constants of the ring have changed more in the former than in the latter radical relative to the initial molecules[52] (Tables 1 and 2).

Quasi-line luminescence spectra have been used to provide the vibrational frequencies of radicals obtained by the photodissociation of durene[79,80], xylenes[81], ethyltoluenes[82-84], and diethylbenzenes[85]. Assignment of the frequencies of the radicals was based on analogy with the vibrational spectra of the initial molecules and of related paramagnetic species.

The vibrational frequencies 630, 1010, and 1600 cm^{-1} observed[86] in the luminescence spectrum of the diphenylmethylene diradical are closely similar to those of benzene (606, 992, and 1600 cm^{-1}).

Table 2. Force constants (10^6 cm^{-2}) of carbon–carbon bonds in toluene and the benzyl radical.

Bond	Toluene	Benzyl
Q″ q	6.77	8.13
Q Q	10.04	10.06
Q Q′	10.04	9.52
Q′ Q″	10.04	9.90

A vibrational structure has recently been given[87] for the fluorescence and phosphorescence spectra of the α-indanyl free radical obtained by the γ-radiolysis of indane frozen in a neutral matrix at 77 K, and assignment of several vibrational frequencies has been attempted by analogy with indane.

The infrared spectrum of the exceptionally stable perchlorodiphenylaminyl radical has been given[88] without any attempt at interpretation.

IV. VIBRATIONAL SPECTRA OF RADICAL-IONS

Radical-ions provide a convenient model for elucidating the influence of an unpaired electron on the force field of a molecule, since the matrices of the kinematic coefficients of a neutral molecule and of a radical derived from it should not differ greatly (the masses are the same, and the distances would not change markedly). The main changes in the vibrational frequencies are therefore determined by variation in the force constants. Until recently only the infrared spectra of radical-ions had been investigated. The first communications on the Raman spectra and the resonance Raman spectra have appeared only during recent years as a result of improvement in the method of obtaining the former spectra and the use of lasers for their excitation.

Papers on the vibrational spectra of radical-ions can be divided roughly into three groups. The most numerous group contains spectra and their qualitative description with an approximate assignment of one or two bands[61,89-101]. The second group[102-126] combines investigations of the frequency shifts in certain characteristic vibrations in a series of radical-ions of similar structure and correlations of these shifts with the variation of the parameters of the electron structure. The third group[127-137] comprises only the most recent publications, which give a fairly complete interpretation of the vibrational spectra of radical-ions based on calculation of the normal vibrations, together with an estimate of the force field and a comparison of the force constants with the parameters of the electronic structure.

Research on the infrared spectra of free radical-ions began in 1954–1955 with the work of Kainer and Otting[61,89], who obtained the spectra of various nitrogen-containing

radical-cations and compared them with those of the corresponding neutral molecules to establish the spectral variation on passing from molecules to radical-cations. The appearance of the unpaired electron in the radical salts of secondary and tertiary *para*-substituted arylamines leads to a marked strengthening of bands in the region of 6.25 μm due to stretching vibrations of the phenyl rings and of the band at 8.5 μm due to CH-deformation vibrations[61]. These effects are considerably weaker in the spectrum of pentaphenylpyrrole perchlorate, but the bands at 6.92 and 7.11 μm have become much more intense[61]. The spectrum of pyocyaninium perchlorate exhibits marked strengthening of the CH bands at 3.3 and 3.4 μm, with the appearance of two bands, at 2.90 and 2.95 μm, attributed to vibrations of OH and NH bonds respectively. With pyocyanin perchlorate it is impossible to distinguish ν(OH) from ν(NH) on the basis of the 3.1-μm band, owing to the bridge between the nitrogen and oxygen atoms[61].

A spectral investigation was made[89] on the radical-ions obtained by reaction between the electron-donating *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) and electron-accepting halogenated *p*-benzoquinone derivatives. The spectrum of the radical-anions shows a decrease in the ν(C=O) frequency to 6.5 μm (from 6 μm for the neutral molecule). The spectrum of the cation is characterised by weakening of the ν(CH) and γ(CH) bands at 3.5 and 12.3 μm, with a marked shift in the $\delta(CH_3)$ band to 7.55 μm, while resembling the spectrum of the cation in the radical salt with the inorganic perchlorate anion (Wurster's blue).

A series of papers by Matsunaga[90-96], containing the infrared spectra of radical salts, must also be included in the first group. He examined the infrared spectra of the anions in the sodium and potassium salts of tetrachloro-*p*-benzoquinhydrone, *p*-biphenoquinhydrone, and tetrachloro- and tetrabromo-*p*-biphenoquinhydrone[90]. Using an approximate relation between the force constant and the bond order together with an empirical dependence of ν(C=O) on the force constant, this worker calculated bond orders $P(C{=}O)$ and force constants for the radical-anions.

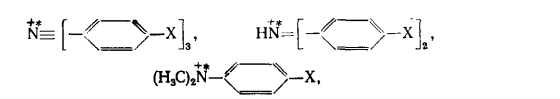
The radical-cations in salts of phenothiazine with iodine and bromine have similar spectra, differing markedly from that of the original molecule[91,92]. The infrared spectra of the radical-cations of dibenzophenothiazine remain unchanged on replacement of chloride by bromide, iodide[93], and also perchlorate anions: i.e. the spectra of the radicals are determined mainly by the absence of an electron from the highest filled orbital and are independent of the nature of the gegenion. The same conclusion applies also to the infrared spectra of the radical salts of phenoxazine, phenoselenazine, and benzophenothiazines with iodine and bromine[94]. Examination of the infrared spectra of the radical-cations of these compounds with halogenated derivatives of *p*-benzoquinone as anions shows[95] that the nature of the radical-cations remains the same with organic and with inorganic anions. From the displacement of the carbonyl band in the spectra of the anions it was concluded that this function loses ~ 30% of its double-bonded character, and the ring loses its quinonoid structure. This explains the marked difference between the infrared spectra of the radical-anions and those of the neutral molecules. The spectra of such radical-anions of semiquinones also resemble those in the alkali-metal salts. The presence of similar semiquinone radical-anions was observed[96] in the infrared spectra of complexes of dibenzophenothiazine with dichlorodicyano-*p*-benzoquinone, of 5,6 : 11,12-bisdithionaphthacene with *o*-chloranil, and of ferrocene with tetrachloro-*p*-biphenoquinone. The radical compounds investigated in this series of papers by Matsunaga have attracted attention as organic semiconductors, and their infrared spectra have been studied in parallel with their electrical conductivity.

In solutions with different gegenions the infrared spectrum of the radical-anion of 7,7,8,8-tetracyanoquinodimethane (TCQM) exhibits a bathochromic shift of $\nu(C{\equiv}N)$ (from 4.50 μm in the neutral molecule to 4.55–4.60 μm in the radical-anion[97]). Comparison of the infrared spectra of the radical salts $[TCQM]^-Li^+$ and $[TMPD]^+ClO_4^-$ recorded in Nujol with the spectrum of $[TMPD]^+[TCQM]^-$ indicates[98] that in the last salt both components are present in ionic form. Raman and infrared spectra have been obtained[99] for radical-ion complexes of tetracyanoquinodimethane with various cations; the spectra were not interpreted, but characteristic intense bands in the range 1100–1300 cm^{-1} were noted.

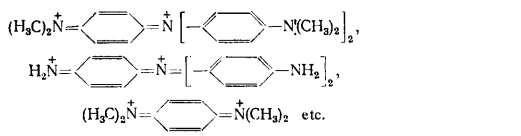
The infrared spectra in Nujol and hexachlorobutadiene of the radical salts—triphenylammonium bromoantimonate, triphenylmethyl chlorostannate, tri-*p*-tolylammonium chloroantimonate, tri-*p*-tolylmethyl hexafluoroniobate, and tri-*p*-tolylammonium hexafluorotantalate—were given[100] without interpretation.

On examining a series of radical-anions obtained from alkylnitrobenzenes with alkali metals in dioxan, Nakai[101] found that the most significant difference between the spectra of the radical-anions and those of the neutral molecules was the enhanced intensity of the band due to antisymmetric nitro-stretching vibrations.

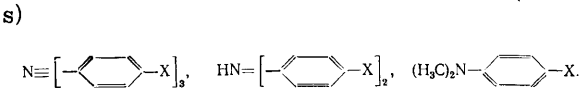
The second group comprises more detailed investigations[102-104] of the infrared spectra of several di- and triarylamine radical-cations



(X = $N(CH_3)_2$, NH_2, OCH_3, F, Cl, NOH, $NOCH_3$) and quinonedi-imine dyes (doubly charged cations)



With certain simplifications a relation was established[102] between the bond order calculated in the Hückel approximation and the stretching frequencies of the bonds attaching the benzene ring to the substituent and to the nitrogen atom in the arylamine radical salts, which explained the rise in these frequencies observed in the cations relative to the neutral molecules. The spectra of the above radicals and dyes were assigned[103,104] on the basis of an interpretation of those of the initial neutral molecules (leuco-bases)



Comparison of the infrared spectra indicates that singly and doubly charged cations are related in structure. Conversion of a radical into a dye does not produce such a marked change in structure as does that of the leuco-base into the radical. The changes observed in the spectra of radicals and dyes relative to those of the leuco-bases suggest that the positive charge appearing on the central nitrogen atom of the cation leads to displacement of the electrons of the lone pairs of the nitrogen, oxygen, and fluorine substituents in the CN, CO, and CF bonds, which are thereby strengthened. The consequent redistribution

of electron density changes the force constants of the CC bonds in the benzene ring. Thorough investigation of ν(C–N) in radicals and dyes, together with data for many other compounds, indicated[104] that the CN bond orders had levelled out.

Savitskii and Kuznetsov[105] have since examined the infrared spectra of the Wurster salts of *p*-phenylenediamine (pPDA), *NN*-dimethyl-*p*-phenylenediamine (DMPD), and *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD). The spectra of the radical salts were assigned by analogy with those of the initial amines and on the basis of the isotopic frequency displacements in the deuterated compounds. The range of skeletal vibrations undergoes the most considerable changes in the spectra of the radical salts in comparison with the initial amines, the frequencies tending to rise presumably owing to the more quinonoid character of the nitrogen–carbon skeleton. In the case of $[pPDA]^+$ and $[DMPD]^+$ hydrogen bonds of the anions (bromide and iodide) and amino-groups of the cations are involved in formation of the crystalline state, with a decrease in the paramagnetism of these salts. In the paramagnetic salt $[TMPD]^+$ the crystalline state is formed without the involvement of hydrogen bonds, obviously owing to steric hindrance.

Radical-anions of conjugated polycyclic hydrocarbons are obtained in high yields and are quite stable in a vacuum, which make them convenient subjects for investigation by infrared spectroscopy. Kachkurova[106–108] examined the infrared spectra of the radical-anions of naphthalene, anthracene, naphthacene, and pentacene, obtained in a vacuum by interaction with a metallic potassium mirror in oxolan. Assignment of the observed bands was facilitated by recording also the spectra of deuterated analogues. The frequencies showed a general tendency to fall on radicalisation, which was attributed to the presence of the unpaired electron in an antibonding orbital, weakening all the bonds in the radical with a decrease in force constants and increase in bond lengths. The frequency shift of the out-of-plane CH-deformation vibrations was especially large. It decreased with increase in the number of rings in the hydrocarbon, owing to the diminished electron density on the carbon atoms. With naphthacene and pentacene dianions could be obtained[108,109]. The effect on certain vibrations of the successive addition of two extra electrons could be traced by comparing the spectra of dianions and monoanions. A further fall in a series of frequencies with increase in the electron density on the ring carbon atoms is observed in the dianion spectra. The frequency shift of out-of-plane CH vibrations is larger for naphthacene than for pentacene, since the extra electron is distributed among a larger number of aromatic rings.

A preliminary assignment of several infrared bands and Raman lines of the radical-anion of naphthalene, observed by other workers[110], is consistent with Kachkurova's results[106,107].

Examination of the structure of the electronic absorption spectra of the radical-cations of naphthalene, anthracene, and phenanthrene in vitreous boric acid[111] gave the ring CC-stretching frequencies as respectively 1485, 1411, and 1356 cm^{-1}, with a fall in frequency in comparison with the neutral molecules. The infrared spectrum of the radical-cation of polyfluorinated naphthalene[112] also showed the disappearance of bands in the range 1600–1670 cm^{-1}, assigned to ring carbon–carbon vibrations, with the appearance of bands at ~ 1550–1590 cm^{-1}. As in the case of the radical-anions[106,107], such fall in frequencies is caused by weakening of the bonds.

The infrared and Raman spectra of the radical-anion of anthracene, obtained as a solid film by coprecipitation of anthracene and potassium vapours in a vacuum, have been investigated[113]. Films having different ratios of potassium to anthracene ($\frac{1}{2}$, 1, and 2) were identified from the vibrational and electronic spectra. Certain frequencies exhibit irregular behaviour, although in general transfer of the extra electron loosens the bonds. It was therefore considered urgently necessary to analyse the force constants both for a real interpretation of the spectra and for a quantitative estimate of the effect of the extra electron. Such irregularity in the frequency shifts was not observed by Kachkurova[106,107], obviously owing to the impossibility of observing the complete spectrum of anthracene dissolved in oxolan.

Resonance intensification of certain bands in the Raman spectrum of the radical-anion and the dianion of anthracene has been observed[114] in oxolan. According to a preliminary assignment no large differences are evident between the solid state and the solution, but the normal coordinates and results for deuteriated compounds must be examined to establish the correctness of the assignment. Later the same workers[115] observed the resonance form of the Raman spectrum of the radical-anion of biphenyl in oxolan. Assignment of the bands was based on analogy with neutral biphenyl. Both positive and negative displacements of the bands were observed. The higher stretching frequency of the central bond was associated with an increase in its order.

The radical-anions of several aromatic nitriles—benzonitrile, 1- and 2-cyanonaphthalene, *p*-cyanobiphenyl, 9-cyanophenanthrene, 1-cyanopyrene, 9-cyanoanthracene, etc.—obtained both by reaction of the nitriles with alkali metals in oxolan[116] and by cathodic reduction in dimethyl sulphoxide[117], showed a fall in the frequency of out-of-plane CH-deformation vibrations on radicalisation. The smallness of the change in polarity of the CH bonds can be judged from the almost identical intensities of these bands in the initial nitriles and in the radical-anions. Radicalisation entails weakening of CC valency bonds and hence a fall in frequency in the region of 1600 cm^{-1} with an increase in intensity. The nitrile-stretching bands $\nu(C{\equiv}N)$ were the most sensitive to the change in structure of aromatic nitriles on reduction. In the radical-anions their frequencies had fallen by 95–140 cm^{-1}, while the half-widths had increased from 7–9 to 22–45 cm^{-1}. The accompanying increase in the integral intensities of the nitrile bands was about tenfold.

The fall in frequency of the nitrile group on the appearance of a further electron in an antibonding orbital of a nitrile dianion[118] is 50% greater than with the singly charged anion. The half-width increases to 50–70 cm^{-1}, while the integral intensity is around hundredfold that observed for the neutral molecule. Such sensitivity of the C≡N vibration to variation in electronic structure gave rise to a broad investigation of the behaviour of nitrile bands on the formation of radical-anions from a number of aromatic nitriles[119,120]. The change in frequency of this vibration gives an indication of the change in order of the C≡N bond and also in its force constant: the shift in $\nu(C{\equiv}N)$ correlates with the decrease in the calculated bond orders $P(C{\equiv}N)$. The intense $\nu_{as}(C{\equiv}N)$ band of aromatic radical-anions containing two nitrile groups is accompanied by the appearance of a weak $\nu_s(C{\equiv}N)$ band at a higher frequency, not allowed in neutral molecules for reasons of symmetry, but active in radical-anions[119] owing to the unsymmetrical disposition of the gegenion.

The infrared bands of radical-anions of ^{15}N-substituted nitriles[120] exhibit smaller isotopic displacement than in the case of the neutral molecules, which indicates that CC bonds adjacent to a nitrogen atom make a greater contribution to the vibrational energy. Inspection of the vibrations of radical-anions containing two nitrile groups leads to the conclusion that conversion of a molecule into a radical produces a considerable increase in vibrational interaction between the separated C≡N groups. The interaction force constant has been estimated on the basis of a simple vibrational model (N≡C–C...C–C≡N) as $F_{CN,CN} \simeq 0.3$ mdyn Å^{-1}. The main factor increasing vibrational interaction in the radical-anions is the great mobility of the unpaired electron in the antibonding orbital.

The carbonyl-stretching frequency provides a convenient indicator of change in the electronic structure of the group. It can be used[121,122] to determine the density ρ of the unpaired electron on the carbonyl group in radical-anions of ketones. The displacement of the carbonyl band in the spectrum of the radical relative to its position in the neutral molecule is described by the equation

$$\Delta\nu(C=O) = A\rho, \qquad (1)$$

where $A = 250$ cm^{-1} is a constant, roughly half the difference in frequency between double and single carbonyl bonds. A similar dependence extends to the nitrile and sulphonyl groups. An attempt to obtain a similar relation for the aryl group was unsuccessful, which the Reviewers regard as normal in view of the complicated form of the ring-stretching vibrations. Formula (1) is extremely useful for assigning the ν(C=O) frequencies of the reduced forms of carbonyl compounds. In particular, this relation formed a guide in interpreting[123] the ν(C=O), ν(C=C), and ν(C≡N) bands in the infrared spectra of the dianion and the radical-anion of biscarbodicyanocyclobutadiene studied in solution in dimethyl sulphoxide. The carbonyl bands showed that the frequency for the radical-anions was on the average ~ 35 cm^{-1} lower than in the neutral molecule, with an additional fall of ~ 43 cm^{-1} on further reduction to the dianion. The density of the unpaired electron on the carbonyl group in the radical-anion estimated by means of formula (1) is 0.17. The nitrile frequencies also fall on passing from the neutral molecule to the radical-anion and the dianion.

The magnitude and the direction of the frequency shifts of the carbonyl bands in the infrared spectra of the radical-anions and dianions of benzophenone, fluorenone, phenanthraquinone, and anthraquinone in polar solvents, on the application of Eqn. (1), give about the same order of magnitude of electron density on the carbonyl group[124] as does calculation to the Hückel approximation. The diminution in double-bonded character of the carbonyl bond with the accumulation of negative charge on the antibonding orbital is reflected in a change in the force constants calculated from the orders of the bonds and their self-polarisabilities by means of the formula of Coulson and Longuet-Higgins.

The infrared region of the carbonyl and aryl frequencies (1800–1500 cm^{-1}) has been examined following the reduction of several diketones on a metallic mirror in oxolan[125]. From the change in these frequencies and in the colour of the solution it was concluded that reduction of the diketones took place in two stages.

In the infrared spectrum of the dianion of tetraphenylethylene[126] the aryl frequency is 36 cm^{-1} lower than in that of the neutral molecule, while ν(C=C) is not observed. The large shift in the aryl frequency together with nuclear magnetic resonance data and quantum-chemical calculations of the electron density suggested an almost planar structure for the dianion and strong delocalisation of antibonding electrons.

In contrast to radical-anions in solution, stable radical-anions in the solid phase give a sufficiently complete spectrum for more reliable interpretation and estimation of the force field. Such investigations have recently been made for the radical-anions of chloranil (p-QCl$_4$)[127], bromanil (p-QBr$_4$),[126,128] 2,5-dibromo-3,6-dichloro-p-benzoquinone (p-QBr$_2$Cl$_2$),[130] and tetracyanoethylene[131,133–135]. All these compounds show significant differences between the spectra of the neutral molecules and those of the radical-anions, probably because of differences in their intramolecular force fields. The influence of the crystal field on the vibrational frequencies was assumed to be small and was disregarded. The radical-anions of the halogenated derivatives of p-benzoquinone were closely similar. In all three compounds the appearance of an unpaired electron in the lowest antibonding orbital was associated with a considerable fall in the stretching frequencies of the C=O and C=C bonds. In a force field this causes a decrease in the force constants of the C=O, C=C, and C–Br bonds (and also of the C–Cl bond in p-QBr$_2$Cl$_2$) with an increase in the force constant of the C–C bond (Table 3).

Table 3. Force constants (mdyn Å^{-1}) of the neutral molecules p-QBr$_2$, p-QCl$_2$, and p-QBr$_2$Cl$_2$ and of the corresponding radical-anions*.

Bond	Neutral molecules			Radical-anions		
	p-QCl$_4$[127]	p-QBr$_4$[128]	p-QBr$_2$Cl$_2$[130]	p-$\dot{Q}\bar{C}l_4$[127]	p-$\dot{Q}\bar{B}r_4$[126]	p-$\dot{Q}\bar{B}r_2Cl_2$[130]
C=O	9.7	9.62	9.62	7.3	7.10	7.10
C=C	6.6	6.67	6.67	6.1	6.26	6.26
C–C	3.0	2.96	2.96	3.5	3.33	3.33
C–Br	—	2.63	2.63	—	2.17	2.17
C–Cl	2.67	—	2.67	2.67	—	2.45

*Q = benzoquinone.

Variation of the diagonal force constants was used to obtain the force field of the radical-anions from that of the neutral molecules. Force constants can be expressed in terms of bond orders and self-polarisabilities by means of the relation of Coulson and Longuet-Higgins. For the homopolar C=C and C–C bonds the self-polarisability term is small, which is apparent in a linear dependence of force constants on bond orders. The bond orders P(C=C) and P(C–C) estimated from known force constants agree with the results of quantum-chemical calculations for p-benzoquinone. For the C=O bond the order does not agree as well with those calculated quantum-chemically, but the tendency for P(C=O) to decrease on passing from a neutral molecule to the radical-ion is maintained here. Bond lengths obtained from the bond orders estimated in this way also agree with those calculated quantum-chemically: the C=O and C=C bonds become longer, but the C–C bonds become shorter.

The distribution of spin density has been obtained[132,129] from infrared-spectral data for the radical-anions of chloranil and bromanil on the hypothesis that the coefficients of the atomic orbitals remain the same in the molecular orbitals of the radical-anions as in the neutral molecules. The resulting spin densities are closely similar in

magnitude to those calculated from the hyperfine splitting constants on oxygen-17 in the electron spin resonance spectrum of the radical-anion of *p*-benzoquinone.

The decisive factor in the infrared frequency differences between neutral molecules and radical-anions is the difference in electronic structure[127-132]. Some difference between the bond orders obtained from the infrared spectra and calculated quantum-chemically may be due to frequency shifts under the influence of the crystal field, whose effect may be different for molecules and for radicals. Furthermore, the matrices of the kinematic coefficients of radical-anions and neutral molecules are not strictly identical, which also may make some contribution to the frequency shifts. Therefore the sets of force constants for radical-anions[127,128,130] are not the only ones possible. But the main conclusions on the electronic structure were based on an analysis of the change in the stretching frequencies, and the above effects can be neglected to a first approximation.

The infrared spectrum of the radical-anion of tetracyanoethylene proved especially interesting[131,133-135]. Apart from the C≡N stretching bands at 2208 and 2183 cm^{-1}, displaced to significantly lower frequencies than in the neutral molecule (2262 and 2230 cm^{-1}), and a very intense band at 1371 cm^{-1}, the spectrum of the radical-anion exhibited no appreciable absorption in the range 600–1300 cm^{-1}, where the most intense bands of the neutral molecule are located: only extremely weak bands are present at 1187 and 970 cm^{-1}, corresponding to the intense bands at 1155 and 959 cm^{-1} due to C–C stretching vibrations in the neutral molecule. Since the 1371-cm^{-1} band could have no other origin, it was assigned to a completely symmetrical vibration of the C=C bond (in the Raman spectrum of the neutral molecule ν(C=C) = 1573 cm^{-1}).

Table 4. Force constants (mdyn $Å^{-1}$) of tetracyanoethylene and its radical-anion.

Bond	Neutral molecule		Radical-anion	
	Ref.131	Ref.135	Ref.131	Ref.135
C=C	6.31	6.59	4.00	4.54
C–C	4.80	5.32	5.23	5.68
C≡N	16.84	17.04	15.70	16.34

The activation theory of Ferguson and Matsen and the hypothesis[134] of vibronic interaction have been used[131,133] to explain such activation of a completely symmetrical vibration in the infrared spectrum and the deactivation of antisymmetric vibrations of C–C bonds. The spectrum of the radical-anion of tetracyanoethylene has been interpreted on these assumptions, an analysis of the planar normal coordinates has been made, and the force constants of the bonds have been estimated in the Ursey–Bradley potential function of a simple field. Table 4 demonstrates the good agreement among results obtained by different workers. It shows that the extra electron in the lowest antibonding orbital of tetracyanoethylene decreases the force constants of the C=C and C≡N bonds and increases that of the C–C bond, so that this bond becomes stronger than C=C. The parallel variation in bond orders estimated from infrared spectral data is consistent with the results of quantum-chemical calculations. Investigation of the resonance Raman spectrum of the radical-anion of tetracyanoethylene[135] confirms the validity of the hypothesis of vibronic interaction and supports the earlier assignment of the infrared spectrum.

Recent conclusions[136,137] on the infrared and Raman spectra of the chloranil anion are consistent with previous results[127], although the inadequacy of varying only diagonal force constants on passing from neutral molecule to radical-anion is noted here. The infrared spectrum of the tetracyanoquinone radical-ion[137] is described satisfactorily by the force field obtained by varying the diagonal force constants of the bonds and the interaction constants of the bonds in the neutral molecule. The change in the latter constants is attributed to rearrangement of the quinonoid ring in the direction of a benzenoid structure.

The possibilities of resonance Raman spectroscopy for investigating free radicals has been demonstrated[138] in a study of the anions and dianions of several aromatic compounds (anthracene, biphenyl, terphenyl, diphenylbutadiene, perylene, and benzophenone). The differences observed in the spectra are larger on passing from the molecule to the anion than from the anion to the dianion. The appearance of several new bands with the charged forms is attributed to change in the selection rules under resonance conditions of excitation. Examination of such spectra is promising for systems having the strongest vibronic interactions, such as free radicals and multicharged ions possessing mobile electrons.

Investigation by the same workers[139] of the resonance Raman spectra of negative and positive mono- and di-ions of naphthacene revealed a considerable change in intensity on passing from neutral molecules to ionic forms, and established that the spectra were influenced mainly by the magnitude of the charge, not its sign.

A brief communication on the resonance Raman spectrum of the radical-cation of *p*-phenylenediamine[140] notes the high concentration sensitivity and the possibility of excluding the interfering effect of the solvent as advantages of the method. The spectrum is interpreted on the assumption of a cation-radical structure with the carbon–nitrogen bonds partly double-bonded in character.

A quite recent careful investigation[141] of the infrared and Raman spectra of the 7,7,8,8-tetracyanoquinodimethane radical salt $Cs_2(TCQM)_3$ and its deuterated derivatives, when compared with the results of X-ray diffraction, leads to the very interesting conclusion that the organic compound is present as two radical-anions and one neutral molecule.

Thus this survey of the literature provides evidence of the usefulness of applying methods of vibrational spectroscopy to investigate the changes of electronic structure involved in the conversion of molecules into radicals.

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