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METHODS FOR PRODUCTION OF RADICAL IONS IN LOW TEMPERATURE MATRICES FOR ELECTRONIC SPECTROSCOPY

Prepared for publication by

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Methods for production of radical ions in low temperature matrices for electronic spectroscopy

Abstract. The methods and techniques of producing radical ions in low temperature matrices are reviewed. The methods are compared and contrasted and recommendations are made where clear differences are found. The properties of various low temperature matrix-forming materials are presented.

INTRODUCTION

Photochemists often encounter absorption and luminescence spectra of radical ions. This occurs, *inter alia*, during the study of electron transfer processes induced by photon- and electron pulse excitation in fluid solution at ambient temperature. In order to facilitate spectral identification of radical ions, it is desirable to produce authentic radical ion samples reliably.¹ Standard methodology is required if published data are to be of use to the photochemical, photobiological, radiation chemical and electrochemical communities at large. It is the purpose of this document to recommend methods for the reliable production and spectral characterization of radical ions in low temperature matrices.

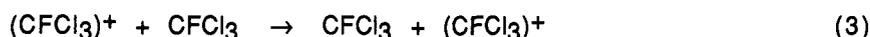
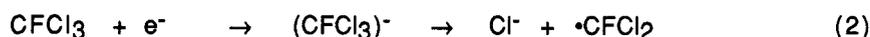
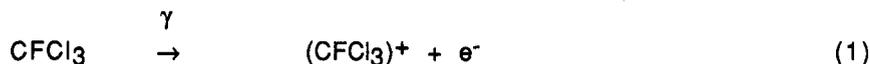
Spectroscopic studies of the generation and trapping of ion radicals were first accomplished by irradiation of triaryl amines in EPA (ether:pentane:alcohol) glass or of aromatic hydrocarbons in boric acid glass with the ultraviolet (UV) light from a high pressure mercury arc. Currently, radical ions are often generated by high energy radiation (e.g. ^{60}Co γ rays) in low-temperature matrices. The first observations of the emission and excitation spectra of radical ions generated by photoionization in rare gas matrices were made in the 1970's. A number of other methods have also been used. Determination of the absorption and luminescence spectra of such radical ions in low temperature matrices is valuable for several reasons. First, complementary to EPR spectroscopy, the spectra provide fundamental information regarding the structure of the radical ions, i.e., how their chemical and electronic structure differ from those of the parent closed shell molecules.² Second, they afford information about the dynamics of electrons and holes in matrices. In this document, methods for generating and characterizing radical ions in low temperature matrices are presented. For more detailed consideration of the subject see reference 3.

METHODS OF GENERATION

Several different techniques are used for low-temperature matrix studies. These methods are summarized below.

Radiolytic Methods. γ -Rays from ^{60}Co ^{3a,b,i,j} or X-rays from a tungsten anode X-ray tube (20-45 kV/25-45 mA),⁴ interact with substances containing elements from the first three rows of the periodic table predominantly via the Compton effect. Highly energetic electrons are ejected, which in turn excite and ionize the molecules. ^{60}Co , obtained by the reaction of ^{59}Co with thermal neutrons, decomposes with a half-life of 5.26 years to ^{60}Ni with emission of γ -rays having an average energy of 1.25 MeV. Since the energy never exceeds 2 MeV, radioactivation of samples *via* a (γ , n) reaction does not take place under these conditions. In some cases, it is sufficient to irradiate the sample directly in the solid state. This could

in principle produce an electron and hole well separated from one another. The formation of $[\text{Mn}(\text{CO})_x\text{hal}]^+$ and $[\text{Mn}(\text{CO})_x\text{hal}]^-$ from $\text{Mn}(\text{CO})_5\text{hal}$ (hal = halogen) crystals is such an example.⁵ In other cases, however, electron return dominates, which makes the authentic generation of the expected radical ions difficult. To overcome these problems, the use of certain glassy solvents, called matrices, was introduced. The chief role of the matrices are not only to isolate and stabilize reactive intermediates, but also to serve as the principal target and the source of migrating electrons and holes that are to be trapped by substrates. They are exemplified by the reactions of fluorotrichloromethane in Eqn 1-4.



Electrons are ejected (Eqn 1) and rapidly scavenged by the solvent halocarbon molecules (Eqn 2). Solvent cations are mobile *via* hole migration (Eqn 3) until they meet a solute molecule M. Reaction (Eqn 4) takes place as long as the ionization potential (E_i) of M is less than that of CFCI_3 (ca. 11.9 eV).

Photoionization or electron-impact ionization in the gas phase and/or on the surface of rare gas matrices.^{3d,3f,3g,6,7} Argon or hydrogen resonance vacuum-UV-induced photoionization (*e.g.*, Lyman α -radiation from a gas resonance lamp) during sample deposition is used to analyze detailed vibronic spectra of polyatomic radical cations. High resolution emission and excitation spectra of emissive radical cations of polyatomic molecules are obtained. Typical examples are provided by halobenzenes and acetylenic compounds. More recently a similar technique has been developed to form ions by means of neon resonance photoionization (*e.g.*, at 16.8 eV) or electron bombardment at the site of deposition on a rare-gas matrix at 4 K. This method has been applied very successfully to EPR spectroscopy of small highly reactive ion radicals, but it has not yet been applied for UV/VIS absorption spectroscopic studies.

Fast ion or atom bombardment.⁸ Substrates at high dilution in argon are deposited at 15 K during simultaneous 2000 eV proton beam irradiation. ^{8a} In this way, CCl_4^+ ($\nu_{\text{max}} = 374 \text{ cm}^{-1}$) was produced and studied by IR spectroscopy. Other atoms (*e.g.*, Ne) and ions (*e.g.*, Ne^+) have also been used, and other radical ions have been prepared by this technique and studied by various spectroscopies (UV/VIS, emission, and EPR). For a leading reference, see 8b.

Photolysis in chlorocarbons in the presence of Lewis acids.⁹ UV irradiation (*e.g.*, a Philips sp 500 high-pressure mercury lamp) of a mixture of alkynes and aluminum chloride in dichloromethane at low temperature, for example, generates the cation radicals of alkynes and cyclobutadienes. Similarly, irradiation in trifluoroacetic acid containing mercury (II) trifluoroacetate is effective.^{9c} The cation radicals generated are often characterized by EPR spectroscopy, but there is no reason why absorption and/or luminescence spectra cannot be taken. Antimony pentafluoride (SbF_5) is often used to generate carbocations at cryogenic temperature and may be of use in generating cation radicals under irradiation.

Multiphoton ionization.¹⁰ Two methods have been used in matrix photoionization. In one technique, a high flux of equivalent low energy photons, *e.g.*, from an argon resonance lamp, is used to ionize molecules directly. In the other, resonance enhanced two photon ionization, the absorption of a resonant photon to excite a molecule to an intermediate state is followed by the absorption of a second resonant photon (usually of different energy than the first) to excite the intermediate state into ionization. Because of the resonant nature of the latter method, it has the potential to produce parent ions extremely efficiently. Since the irradiated solutions contain no paired counterions, they are necessarily thermodynamically unstable and the ions disappear upon warming. Care must be taken not to allow the temperature of the irradiated sample to rise until the spectral measurement is finished. The disappearance of the signals on thawing may be used for confirmation of the signal assignment.

High energy electrons from an accelerator.¹¹ When N₂O-saturated solutions are irradiated with short pulses of high energy electrons (ca. 4 MeV), HO· radicals are generated in aqueous solutions and radical cations are formed in hydrocarbon solvents.

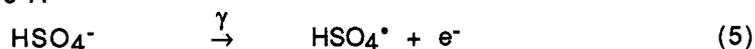
Alkali and alkaline earth metals. Potassium or sodium-potassium alloy in an ether solvent, *e.g.*, 1,2-dimethoxyethane (DME), tetrahydrofuran (THF) or 2-methyltetrahydrofuran (MTHF), are the most convenient reagents for generating radical anions. Whereas MTHF makes a glass (at -196°C) suitable for optical studies, DME and THF are not always sufficiently transparent. The anion spectra of substrates are measured at -196°C.^{3a} Dianions and trianions can be generated in this way.¹²

MATRIX MEDIA

Solidified inert gasses, glassy solids of mineral acids, organic solvents, and polymer films are typically used as matrix media. The choice of matrices depends critically on the phenomenon to be examined. The chemical behavior of the trapped ion radicals is modified by the "cage effect", which generally prevents the diffusion, particularly of large molecular ions, from the trapped site. As a result, unimolecular processes not requiring diffusion are enhanced with respect to bimolecular reactions or processes requiring separation of reactive fragments. On the other hand, electrons can move relatively unhindered through the matrices, especially in the rare gas solids. The properties of various media are reviewed below.

Mineral acids. Boric acid was one of the first matrix media used for these purposes.¹³ Orthoboric acid, H₃BO₃, is heated at 240°C until a stoichiometric amount of water is removed. The metaboric acid, (HBO₂)_x, obtained is the lowest melting material suitable for use as a glassy matrix.

Sulfuric and phosphoric acids are also used as solvents for the radiolytic generation of radical cations. The basis of the method is outline in the reactions of Eqn 5-7.¹⁴



Since HSO_4^\bullet radicals are rigidly trapped at 77 K (H_2SO_4 $T_f = 283.51$ K), reactions (5-7) occur generally only on annealing. This solvent is used complementarily to Freons; compounds that are insoluble in Freon or dissolve as dimers or aggregates therein could be soluble in these mineral acids. Successful examples include R_3N^+ , from R_3N^+ , R_3P^+ from R_3PH^+ ions, and $(\text{CH}_3\text{SSCH}_3)^+$ from dimethyl disulfide. Otherwise, the utility of these solvent systems is limited.

Simple alkyl halides and Freons. Many haloalkanes (e.g., CFCl_3 , $\text{CFCl}_2\text{CFCl}_2$, and the mixture of CFCl_3 and $\text{CF}_2\text{BrCF}_2\text{Br}$) form glasses suitable for generation of radical cations.¹⁵ Carbon tetrachloride, mixtures of *n*-*orsec*-butyl chloride and isopentane were first introduced by Shida and Hamill.^{15a} These matrix media form glasses which remain hard near 77 K where the Freon glasses begin to allow diffusion. However, C-H vibrational overtones obscure the near infrared region of the spectrum (1100-1600 nm) and a special grade of butyl chloride (protein sequence grade from Merck) must be used to obtain good glasses. These halogenated materials are often useful as additives to a rare gas matrix or a polymer film (*vide infra*). Sandorfy discovered that a 1:1 (v/v) mixture of Freon-11 (CFCl_3) and Freon-114B2 ($\text{CF}_2\text{BrCF}_2\text{Br}$) forms a stable clear glass at 77 K suitable for spectroscopic studies.^{15b} Since then various kinds and combinations of Freon solvents (CF_3CCl_3 and $\text{CFCl}_2\text{CF}_2\text{Cl}$) have been found to be effective. Freons have considerable generality and wide applicability, since many organic substrates have ionization potentials sufficiently lower than that of the Freons so that Eqn 4 (above) is exothermic in these media. Some comparison of Freon solvents is found in reference 15e. Typical halocarbons such as CCl_4 ($E_i^a = 11.47$ eV) and CFCl_3 ($E_i = 11.9$ eV) are only partly satisfactory for generating the cation of ethane ($E_i^a = 11.49$ eV).

Freon media are of the "solid rotator" type and EPR spectra taken for cations in these matrices are isotropic and show sharp hyperfine splittings. Cation radicals generated in $\text{CFCl}_2\text{CFCl}_2$ are said to have higher mobility compared to other matrix materials. This appears to do more harm than good in matrix isolation electronic spectroscopy. Because of the complexity of the site structure, the absorption and luminescence spectral resolution of radical ions generated in these media is lower than that obtained in rare-gas matrices.

Table 1 lists freezing (T_f) and boiling (T_b) points of several haloalkane glass forming materials.

Rare gases.^{3d,3f,4,6,7,8,10} Rare gases are considered to be slow baths. It is usually the case that, at a given temperature, the rare gas matrices become harder and the lifetime of a reactive intermediate in them becomes longer as one descends the periodic table. Since the lattice constants and therefore the cavity size

Table 1. Properties of Haloalkane Matrices.

Haloalkane	T_f (K)	T_b (K)
CFCl_3	162.67	296.78
$\text{CFCl}_2\text{CFCl}_2$	299.70	366.0
$\text{CF}_2\text{BrCF}_2\text{Br}$	162.7	320.41
CF_3CCl_3	287.2	318
$\text{CFCl}_2\text{CF}_2\text{Cl}$	236.8	320.78
<i>n</i> - $\text{C}_4\text{H}_9\text{Cl}$	150.1	351.58
<i>sec</i> - $\text{C}_4\text{H}_9\text{Cl}$	159.9	341.40

Table 2. Properties of Rare Gas Matrices

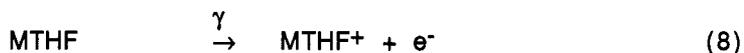
Matrix	T_m (K)	$0.4T_m$ (K)	$R(A)^a$
Ne	24.48	9.8	4.464 (4.25 K)
Ar	83.95	33.6	5.311 (4.25 K)
Kr	116.55	46.6	5.721 (58 K)
Xe	161.25	64.5	6.197 (58 K)

a.) Lattice constant of the cubic close-packed structure

increase from Ne to Xe, the choice of the best rare gas also depends on the size of a substrate molecule. At temperatures equal to 0.4 x the melting points of the matrix, comparable mobilities in the rare gas matrices are said to occur (Table 2).

The high ionization energies of argon (15.759 eV) and neon (21.564 eV) permit the trapping of organic molecular cations having large electron affinities. Neon has extreme chemical inertness, low polarizability, and a large conduction band gap which make it an ideal host for isolating highly reactive cation radicals. It is not true that ions are "free" in rare-gas matrices. Rather, they are "solvated" with binding energies near 1-2 eV. Generation of ion radicals and prevention of the immediate electron-hole recombination can become a problem in this matrix unless high energy irradiation or prior generation of the ions, as developed by Andrews^{6b} and Knight,^{6c} is employed. More conveniently, rare gases containing a very small amount of CH₂Cl₂ (e.g., sample: CH₂Cl₂:Ar = 1:2:2000) or other alkyl halide (including Freons) are recommended for studying vibronic absorption spectra of radical cations.^{4,10a} Doping of rare gases with a small amount of an amine permits the study of radical anions in selected cases, e.g. where the electron affinity is high.

2-Methyltetrahydrofuran. 2-Methyltetrahydrofuran (MTHF) forms a transparent glassy solid at 77 K ($T_f = 136.0$ K, $T_b = 353.1$ K) which is suitable for generation of radical anions. The most important sequence of reactions after γ -irradiation in this solvent are shown in Eqn 8-10.



Electrons ejected through interaction of MTHF and γ -rays (Eqn 8) travel through the bulk of the rigid solution until they encounter a solute molecule of sufficiently high electron affinity to produce the corresponding radical anion (Eqn 10). Otherwise, the electrons eventually come to rest in the intermolecular vacancies of the matrix. Holes do not move very extensively and are trapped by matrix molecules (Eqn 9).¹⁶

Alkanes and Shipol'skii solvents. Shipol'skii solvents are popularly used to obtain well resolved vibronic spectra of neutral closed-shell molecules. Ionization potentials of naphthalene and phenanthrene are estimated to be lowered by 1.1 eV in polyethylene and 0.9 eV in methylcyclohexane relative to the gas phase. Polycrystalline "rotator solids" like neopentane (T_f 256.57 and T_b 282.65 K), tetramethylsilane (T_f 171.03 and T_b 299.79 K) and adamantane (T_m 541.1 K) have been used to study UV/VIS spectral of radicals. They also afford well-resolved EPR spectra. Whereas 3-methylpentane (T_f glass and T_b 336.432 K) was often used as a solvent in early radiolysis studies, alkanes possess no special merit for trapping and measuring electronic spectra of radical ions. When radiolyzed at 4.2 K, 1-alkyl radicals are selectively formed as primary products in crystalline, neat *n*-alkanes.¹⁷ The solvent trapped electrons decay spontaneously in 3-methylpentane.

Polymer films.¹⁸ Polymer films doped with a substrate can be prepared by polymerization of the monomer or casting a solution of the polymer containing the substrate, or by soaking a polymer film with the sample solution. In the latter case, a combination of poly(vinyl alcohol) film and *sec*-butylamine solvent has been found suitable for preparation of radical anions, whereas poly(vinyl chloride) film and an alkyl halide or CCl₄ system is recommended for generation of radical cations.

Polymer films are well suited for study of transition metal complexes.^{18c} These substrates are involatile and not amenable to study in gas matrices. They are often insoluble in organic solvents as well. Alkali halide discs, sometimes used for metal complexes, do not necessarily isolate individual ions.

Among polymer membranes, Nafion® (a perfluorosulfonic acid polymer) is unique in that absorption and luminescence spectra of protonated substrates are obtained. Effects of ionizing radiation in these films or membranes will be worthy of study.¹⁹

Sulfur hexafluoride.¹⁷ Gaseous mixtures of sulfur hexafluoride (SF₆) ($T_{\text{sub}} = 209.4$ and $T_{\text{m}} = 222.4$ K) and samples (0.5-1 mol%) are frozen into a quartz cell at cryogenic temperature. An electron ejected by the ionizing radiation is captured by SF₆ forming SF₆⁻. The positive charge transfer takes place from the matrix to substrates that have E_i higher than 11.9 eV but lower than that of SF₆ ($E_i^{\text{SF}_6} = 15.69$ eV). Halocarbon matrices such as CCl₄ and CFCI₃ have been found to be only partly successful to effect generation of the cation of ethane, but generation of this ion is facile in SF₆. The matrix also serves as an excellent heat bath but it does not effect the rate of intersystem crossing of the solute molecules.

Synthetic zeolites and silica. These solid supports have been used to generate radical ions from adsorbed substrates by radiolysis. EPR evidence for the formation of alkane radical cations followed by ion-molecule reaction to give 1-alkyl radicals has been obtained.²⁰ While a special technique, e.g., diffuse reflectance spectroscopy has to be employed for the measurement of absorption spectra under these conditions, luminescence spectra may be obtained normally. Chemiluminescence of tetramethyl-1,2-dioxetane supported on zeolite is documented.²¹ Polyene cation radicals are stabilized so that they can be studied spectroscopically within the pores of activated zeolites.²²

Distinction between radical cations and anions can be problematic, since the spectra of both radical ions derived from alternant hydrocarbons should be similar. The problem can be resolved by several ways. Their magnetic circular dichroism spectra are mirror images. Alternatively, organic halides will trap electrons very efficiently in the matrices, and, therefore, the addition of less than 1% CCl₄ completely suppresses the characteristic spectra of alternant hydrocarbon radical anions in MTHF or ethanol. Since no absorption remains which could possibly be attributed to the radical cations, it may be concluded that there is little or no hole migration in these matrices.^{3a}

Individual matrices yield slightly different solvent shifts as a result of their different polarity.²³ In a given matrix, the solvent induced red shift decreases with increasing size of the radical cation. Increasing the space for hole delocalization appears to decrease interaction of the radical ions with the medium.

SAMPLE PREPARATION AND IRRADIATION

Matrix materials must be purified prior to use. One of the favorite solvents, MTHF, for example, contains a ca. 1% phenolic stabilizer which must be removed. Passage through basic alumina will in general be sufficient. All samples should be prepared under vacuum since O₂, even at small concentrations, traps electrons efficiently. This precaution is less important when cations are to be examined.

To obtain crack-free glasses, a mixture of water and ethyleneglycol (EG) (e.g., 1:1) or ethanol, for example, are recommended to be rapidly cooled down to 160 K and then at 20 K/h to 125±1 K for EG and 92±1 K for ethanol.^{24c}

Polyenes and aromatic hydrocarbons have a tendency to form dimer cations. In order to exclude the complication of observed spectra due to this phenomenon, the concentration of the sample should be lower than 10mM,⁶ or hard matrix media should be employed.²⁴

When rare gases condense on cold surfaces, the heat of condensation raises the temperature of the cell wall. As a result, there is a possibility that the matrix-isolated sample formed at the initial stage of an experiment might be disturbed by the condensation of the matrix gases at a later stage. In order to avoid this phenomenon, controlled depositions of rare gases and/or samples are highly desirable. A state-of-the-art method employs the pulsed supply of the gases through a computer-controlled electromagnetic valve, though this is not recommended if aggregates tend to form. A pulse width of ~10 ms and a pulse interval of ~10 s are used.

⁶⁰Co γ rays are used for high energy irradiation.^{3a,3i} If the rate of spontaneous decay of the color center is appreciable, the dose rate, which is typically ca. 10^{18} eV/g min, may not be sufficient. The yield of solute anions is proportional to absorbed energy (dose) over the useful working range. This may not necessarily be so for the yield of cations. The concentration C of the radical ions thus formed can be estimated by use of Eqn 11, where G is defined as the yield of radical ions produced by 100 eV

$$C(\text{mol/l}) = 10 G I t d N_A^{-1} \quad (11)$$

of absorbed energy, I is the radiation dose rate (eV/g min), t is the irradiation time (min), d is the density (g/cm³), and N_A is Avogadro's number. A G value usually increases with increasing substrate concentration and reaches a well-defined plateau, the typical limiting value being 2-3. Therefore, if $I = 10^{17}$ - 10^{18} (corresponding to 0.1-1 Mrad/h), irradiation of 30 min produces radical ions to a concentration of 10^{-4} - 10^{-3} M. If the initial concentration is 10^{-2} M as is often the case, the conversion from M to M⁺ is 1-10%. Therefore, if the concentration of radical ions is known, the molar absorptivity of the same radical ion generated chemically is known, the G value may be determined on the assumption that the molar absorptivity should not differ under the two conditions. The d values of MTHF, sec-butyl chloride and CFCI₃/CF₂BrCF₂Br (1:1, v/v) are 1.06, 1.09 and 2.28, respectively at 77 K. The G value of the scavengeable electrons for MTHF and those of the holes for the last two solvent systems are 2.55, 3.25 and 2.09, respectively. Since it is difficult to remove hole-scavenging impurities from butyl chlorides, evaluation of molar absorptivity of a cation radical in these solvents based on G = 3.25 is not recommended.

Freons are not at all inert under radiolysis; Eqn 2 above represents one of the typical degradation reactions. Short and long wavelength absorptions due to the fragments from the solvents appear at high absorbed dose of ca. 7.5×10^{19} eV/g. These absorptions may be photobleached without interfering with the absorption of the substrate radical ions.²⁵ The dose rate, radiolysis duration time, and temperature of irradiation should be reported.

Vacuum UV irradiation of guest molecules in rare-gas matrices is performed as follows: A mixture of hexafluorobenzene and argon gas (ca. 1:2000) is deposited on a sapphire window cooled to 4.2 K. Ca. 1 mmole of substrates are deposited over 1-2 hr and irradiated subsequently using a gas resonance lamp for 0.5-2 min.

"Color centers" due to the formation of radical ions are often susceptible to photobleaching. Therefore, the irradiated matrix sample should be protected from ambient light (*vide infra*).

SPECTRAL MEASUREMENTS

Once the desired ions are generated, their low temperature matrix electronic spectra are subject to the methodology and standards for reporting data of molecular absorption and luminescence spectroscopy. Transient kinetics can be obtained by the techniques of pulse radiolysis.^{11,16,26} Polarized absorption spectra are conveniently obtained in stretched polymer films.¹⁸ Since measurements are often made relative to air, and since cracked glasses result in rising background absorption approaching the UV region, the spectrum of the sample must be scanned prior to as well as after irradiation and difference spectra calculated.

Low temperature UV/VIS absorption spectra in a transparent, highly viscous or solid matrix at temperatures below 100 K have been discussed briefly in an IUPAC document:²⁷

"Highly structured spectra can be obtained when the UV/VIS absorption of a solute in certain polycrystalline matrices (e.g. *n*-alkanes, cycloalkanes, inert gases such as rare gases) is measured at low temperatures. For all spectra the solvent, solvent temperature and solute concentration should be specified."

Standards for fluorescence quantum yields in matrices or low temperature glasses have been also discussed.²⁸

On the other hand, there are some additional phenomena and techniques characteristic of the low temperature matrix electronic spectroscopy of radical ions (e.g. photobleaching and recombination luminescence)^{3a} for which nomenclature, standards and/or guidelines are needed.

PHOTBLEACHING AND RECOMBINATION LUMINESCENCE (ref. 29)

Optical excitation of color centers in γ -irradiated glasses may induce migration of electrons and holes leading to the transfer of sites (of the same or different type) and to charge recombination. Solvent-trapped electrons, for example, absorb at $\nu_{\max} \sim 7700 \text{ cm}^{-1}$ ($\lambda_{\max} \sim 1300 \text{ nm}$) in MTHF at -196°C and $\nu_{\max} = 18500 \text{ cm}^{-1}$ ($\lambda_{\max} = 540 \text{ nm}$) in ethanol. These absorptions can be photobleached. When biphenyl is added, absorptions due to formation of its anion radical increase at the expense of the photobleached absorptions. The monochromatized beam of the spectrophotometer, with the high intensity lamp, can be used to measure quantum yields of bleaching and also to induce recombination luminescence. When γ -irradiated 3-methylpentane ($2.7 \times 10^{18} \text{ eV/mL}$) is bleached at 950 nm, the initial quantum yield is almost unity. The efficiency diminishes steadily as bleaching progressed. Exposure even to the spectrophotometer light beam must be minimized to avoid measurable bleaching.

When matrices of some solutes in 3-methylpentane are γ -irradiated and subsequently illuminated at -196°C with 800-2000 nm light, or warmed slightly, they luminesce brightly. These emission spectra are due to the recombination of photoelectrons with cations and correspond to the reported phosphorescence spectra of the solutes. Delayed fluorescence due to electron-cation recombination can be observed on annealing of matrices.^{3a,29}

STANDARDS AND REPRESENTATIVE DATA (ref. 1)

Representative UV/VIS spectral data are given in Tables 3 and 4. The spectral compendium by Shida^{3m} should also be consulted.

Table 3. UV/VIS Absorption Spectral Data for Radical Cations Obtained By Radiolysis In Frozen Matrices At Cryogenic Temperature

Radical Cation	ν_{\max} (cm ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)
1,3-Butadiene ^a	16390	(0.15)
	33880	(1.0)
1,3-Butadiene ^{a'}	18300	1040
	3390	3700
β -Carotene (all <i>trans</i>) ^b	9615	
Naphthalene ^c	14810	24900
	21700	14000
	26240	6000
	32510	40500
	36420	46000
Biphenyl ^c	14920	12000 (+1000)
	26120	56000 (+6000)
<i>trans</i> -Stilbene ^d	13108	5000
	20695	33400
N,N-Dimethylaniline ^e	21460	4400
	29940	8200
	30770	7300
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine ^f	15750	19300 (+200)
	17390	16100 (+100)
	30770	23400 (+800)
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine ^{f'}	16000	18800
	17500	15800
Chlorophyll a ^g	11980	7000

a) Origin bands in Ar/CH₂Cl₂ (1000:1). Relative absorbances in parentheses (ref. 4a).

a') In CFC₁₃/CF₂BrCF₂Br (1:1) at 77 K (ref. 3m).

b) In hexane (ref. 34).

c) Origin bands in Ar/CH₂Cl₂ (300:1) at 20 K (ref 10).

d) In CFC₁₃/CF₂BrCF₂Br (1:1) at 77 K (refs. 15f, 30).

e) In water /ethyleneglycol (1:1) at 125 K (ref. 23c).

f) In 3-methylpentane at 77 K (ref. 31).

f') In CFC₁₃/CF₂BrCF₂Br (1:1) at 77 K (ref. 3m).

g) In *sec*-butyl chloride at 77 K (ref. 32).

Table 4. UV/VIS Absorption Spectral Data for Radical Anions Obtained By Radiolysis In Frozen Matrices At Cryogenic Temperature

Radical Anion	ν_{\max} (cm ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)
β -Carotene (all <i>trans</i>) ^a	11364	
Naphthalene ^b	11560	
	12820	
	21510	
	21980	
	22990	
	27030	30000
Biphenyl ^b	15150	
	24390	37000
	25320	
	26320	
<i>trans</i> -Stilbene ^c	14486	14100
	20030	65700
Benzophenone ^d	12500	10500 ^e
	29400	20100
	30400	17000
Chlorophyll a ^f	12660	11000

a.) In hexane (ref. 34).

b.) In MTHF at 77 K (ref. 3a).

c.) In CFC₁₃/CF₂BrCF₂Br (1:1) at 77 K (refs.15f, 30).

d.) In MTHF at 77 K (ref. 33).

e.) Molar absorptivity data from ref. 3m.

f.) In MTHF at 77 K (ref. 32).

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- ESR spectral data of hundreds of organic ion radicals are compiled (see for example, Landolt-Bernstein's Numerical Data and Fundamental Relationships in Science and Technology, Springer Verlag, West Berlin, 1980, New Series, Group II Vol. 9, Part d1 p. 708 and Part d2 p. 6), but very few compilations of absorption and luminescence spectral data are available, except for the newest one.^{3m}
- One of the subjects of interest is whether the excited states of radical ions are so-called "Koopmans" states or not (see ref. 3i and 4a).
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