Review Article

Structure and Properties of Hydrocarbon Radical Cations in Low-Temperature Matrices as Studied by a Combination of EPR and IR Spectroscopy†

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Use of IR spectroscopy (as a supplement to EPR) may provide new insight into the problem of analysis of structure and properties of organic radical cations. In this work, the results of combined EPR/IR studies of the formation, structure and properties of hydrocarbon radical cations in halocarbon and solid rare gas matrices are discussed. Both IR and EPR studies were carried out with matrix deposited samples irradiated with fast electrons at 15 or 77 K. IR spectroscopic data were found to be helpful in three aspects: (i) characterization of the conformation and association and molecule–matrix interactions of the parent molecules; (ii) identification of diamagnetic products of the reactions of radical cations in ground and excited states; (iii) determining the characteristics of vibrational spectra of the radical cations, which are of primary interest for analysis of chemical bonding and reactivity of the radical cations. The applications of the combined approach are illustrated with examples of studies of several alkenes in Freon matrices and alkanes in solid rare gas matrices. The matrix effects on trapping and degradation of radical cations were interpreted as the result of variations in matrix electronic characteristics (IP, polarizability) and molecule–matrix interactions.

Hydrocarbon radical cations occur as principal intermediates in various oxidative processes (e.g., radiolytic, photochemical, electrochemical, catalytic). Impressive progress in the studies of highly reactive aliphatic radical cations in condensed media has been connected with the use of the Freon matrix technique introduced by Shida and Kato.[1] This technique is based on the radiolytic generation of the radical cations in halocarbon matrices at low temperatures. Fluorochlorocarbons (Freons) were found to be the most suitable media for EPR spectral studies of radical cations. These studies provided unique information concerning the structure and reactivity of primary radical cations, which otherwise would be difficult to obtain.[2,3]

In recent years, several attempts have been made to develop other approaches to the EPR studies of reactive radical cations. In particular, very small organic cations were characterized by EPR in a neon matrix[4–6] (this matrix had previously been used for the study of inor-

ganic radical cation species[7]). The results obtained were important for quantum chemistry and astrophysical aspects; however, the neon matrix method has not been applied to larger organic cations. I am not aware of any successful attempt to record the EPR spectrum of a moderately sized aliphatic radical cation in an argon matrix, which is commonly used for optical matrix isolation studies.[8] Qin and Trifunac[9] reported the EPR spectrum of 1,1,2,2-tetramethylcyclopropane radical cation generated in a xenon matrix doped with electron scavengers; however, this method has not been tested for other organic cations. On the other hand, extensive investigations of the radical cations in zeolite hosts have been carried out by several groups.[10–14] These studies were related to catalysis as well as to radiation chemistry; generally speaking, zeolites appear to be attractive matrices for studies of selective reactivity of radical cations. The problem is to make an appropriate choice of a zeolite host from structural and chemical points of view. It should be noted that zeolites (unlike Freons and solid rare gases) are not suitable for optical studies, which

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may be essential complementary techniques to EPR spectroscopy.

Overall, the Freon matrix technique is the most common method of obtaining information concerning the electronic structure, spin density distribution and reactivity of unstable aliphatic radical cations. Nevertheless, some important features of the trapping, relaxation and chemical reactions of the radical cations in Freon matrices are not well understood. For this reason, application of the results obtained in Freons for the interpretation of the behaviour of the radical cations in various systems is still a topic of discussion. The following issues should be considered in detail.

(1) Very little is known about the state of the parent molecules in a Freon matrix prior to ionization (i.e., molecule conformation, aggregation, molecule–matrix interactions). This aspect is especially important since these factors appear to control the reactivity of the radical cations. Obtaining more information about the state of a solute molecule and its local environment may provide the key to understanding intriguing matrix effects on the properties of the radical cations in Freon matrices.

(2) Only paramagnetic products of thermal and photochemical reactions of the radical cations can be detected by EPR spectroscopy. Lack of information about the reaction products prevents researchers from drawing definite conclusions concerning reaction mechanisms.

(3) EPR studies have revealed a remarkable correlation between the spin density distribution in radical cations and the selectivity of their deprotonation.[15–19] However, to make this a general correlation, it is important to learn more about the nature of chemical bonding in the radical cations. In addition to theoretical work, it would be of interest to obtain essential experimental characteristics of specific bonds (such as force constants), which could be compared with the spin density distribution.

Evidently, the problems under consideration cannot be solved within the framework of the conventional 'Freon–EPR' approach. Several years ago we suggested the use of IR (vibrational) spectroscopy as a supplement to EPR in order to obtain more information from the experiments in Freon matrices.[20] IR spectroscopy is a powerful method for obtaining information about neutral and ionic species regardless of their magnetic properties. In principle, IR spectroscopy is sensitive to molecule conformation and environmental effects (such as solvation, association). Furthermore, vibrational spectra of radical cations can provide valuable information concerning bond properties in ionized species (indeed, it is understood that strict interpretation of these spectra is a specific problem requiring much calculational effort and treatment of the environmental effects).

The proposed combination of EPR and IR spectroscopy was aimed initially at specific studies of the role of radical cations in the radiation chemistry of hydrocarbons. The studies were carried out mainly with simple

alkenes and alkanes in Freons. Recently we were able to extend our approach to studies of the formation and properties of the hydrocarbon radical cations in solid rare gas matrices, which seems to be a more general way to obtain basic characteristics of radical cations.

Screening of the available literature did not reveal any other systematic attempts to apply IR absorption spectroscopy to studies of organic radical cations in Freon matrices. On the other hand, very recently at least three groups have reported the results of extensive studies of vibrational spectra of the radical cations of several hydrocarbons generated by various techniques in an argon matrix.[22–27] However, up to now these studies were restricted to polycyclic aromatic systems of astrophysical interest[21–25] and to conjugated systems.[26,27] None of these studies were compared with EPR investigations of the same systems.

The purpose of this report is to give an outline of our combined spectroscopic approach to the studies of radical cations, including experimental basis, main results and problems and prospects of development. First, the principles of our approach and experimental features will be considered. Second, the results of earlier studies using the Freon matrix technique will be reviewed. Finally, the results of recent experiments with solid rare gas matrices will be presented.

Combined spectroscopic studies: principles and apparatus

The idea of our approach was to make direct thorough comparison between the transformations occurring in the IR spectrum of the system considered and formation and behaviour of the radical cation monitored by EPR. Analysis of the literature shows that the combination of these techniques has not been commonly used in studies of active species generated by ionizing radiation at low temperatures, in spite of the great potential value of this approach. One possible reason for this neglect is concerned with technical problems. Indeed, to make a valid comparison, one should create similar conditions for sample preparation and irradiation in the very different apparatus configurations for IR and EPR studies at cryogenic temperatures. In fact, this implies the construction of two kinds of specific cryostat for radiation-chemical studies (a variant will be considered below). Another reason may result from the widespread opinion that IR spectroscopy is a rather insensitive technique, which requires the use of high doses of irradiation to obtain detectable concentrations of the radiation-induced species. However, this limitation is not so important when using modern FTIR spectrometers with a high signal-to-noise ratio. In our studies we used a Perkin Elmer 1710 FTIR spectrometer and a standard X-band EPR spectrometer.

As mentioned above, the problem of similarity of experimental conditions is of primary significance for the proposed studies. In early work,[20] we carried out a
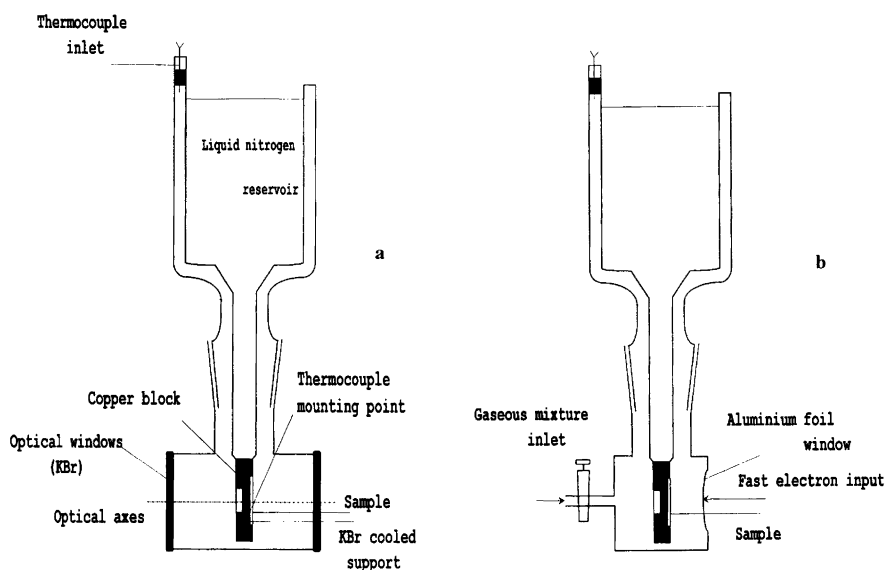
Fig. 1. Schematic representation of the liquid nitrogen cryostat for IR spectroscopic studies of electron irradiated samples at 77–300 K. Two projections are shown. The sample holder is rotated to take the positions for (a) spectral measurement, (b) electron irradiation, or sample deposition (opposite to b).

simple comparison of the results of EPR studies of irradiated frozen Freon solutions (in glass ampoules) and IR studies of the samples obtained by matrix deposition techniques. In preliminary terms, this seems to be acceptable. However, this approach is questionable in our case since we are interested in the fine details of intermolecular interactions, association, molecule conformation, etc. Indeed, the frozen Freon solutions commonly used for EPR studies, in many cases exhibit polycrystalline rather than glassy patterns. Virtually nothing is known about the structure of these frozen solutions, solute molecule distribution, aggregation and microphase separation. In some cases, the sample preparation procedure may have a marked effect on the cation formation and its properties.[28] On the other hand, the matrix deposition technique, which is used in classic matrix isolation experiments, appears to yield reproducible transparent layers of uniform structure. For this reason we chose the matrix deposition technique for sample preparation in both IR and EPR studies. This procedure is suitable for experiments with both Freon and solid rare gas matrices.

Ideally, it is desirable to carry out combined studies by two different spectroscopic techniques in the same cryostat, as was the case for IR–UV studies of the radical cations.[21–23,26,27] However, such experimental design is virtually impossible for IR–EPR studies. Our task was to make two parallel experiments with EPR and IR cryostats using the same gaseous mixture, similar procedure for sample deposition and similar irradiation configuration.

Figs. 1 and 2 are schematic representations of liquid nitrogen cryostats for IR and EPR spectroscopic studies of deposited samples irradiated at 77 K. The cryostat for IR spectroscopic studies of radiation-chemical effects at
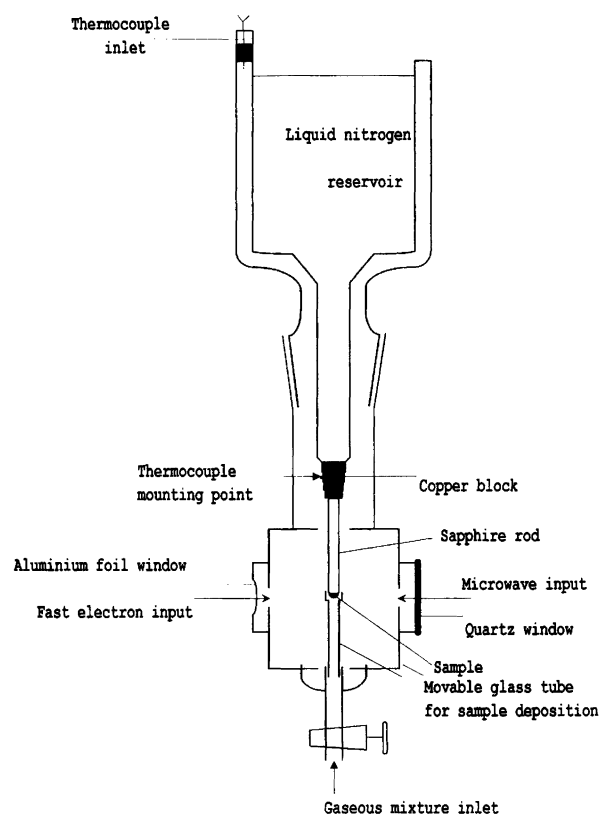

Fig. 2. Schematic representation of the liquid nitrogen cryostat for EPR studies of electron-irradiated samples at 77–300 K.

low temperatures has been used in our laboratory for many years,[29] while the EPR cryostat with vacuum resonator was constructed recently specifically for the studies of radical cations. In both cases, the gaseous
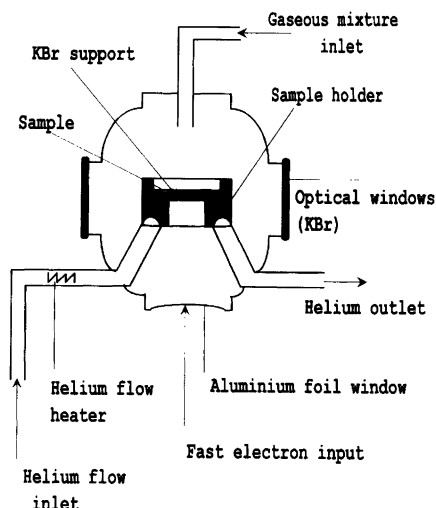
Fig. 3. Schematic representation of the continuous-flow helium cryostat for IR spectroscopic studies of electron-irradiated samples at 10–300 K. The sample holder is rotated to take positions for sample deposition, electron irradiation or spectrum measurement.

Fig. 4. Schematic representation of the continuous-flow helium cryostat for EPR studies of electron-irradiated samples at 10–300 K.

mixture was deposited onto cooled surface (KBr window in the case of the IR cryostat or sapphire rod in the case of the EPR cryostat). The deposited samples were irradiated with fast electrons through a special aluminium foil window in each cryostat. The spectral measurements were carried out at 77 K; the samples can be annealed at any required temperature within the range 80–300 K. This cryostats couple is used for combined EPR–IR spectroscopic studies of radical cations in Freon matrices.

Figs. 3 and 4 illustrate the set-up of the continuous-flow helium cryostats for EPR and IR spectroscopic studies of electron-irradiated samples, which operate at 10–300 K. In this case, the sample is cooled with cold helium gas evaporated from a liquid helium Dewar vessel (101). Typically, the sample irradiation and spectral measurements were carried out at 10–20 K. Use of a helium flow heater makes it possible to anneal the sample at any required temperature over the range 10–300 K. Other principles of these cryostats are essentially similar to those used in liquid nitrogen cryostats described above. The new version of our IR spectroscopic cryostat also has two additional quartz optical windows, which can be used for UV–VIS spectroscopic studies and for photochemical experiments. The helium flow cryostats were used in our experiments with solid rare gas matrices. The temperature of sample deposition was specially adjusted to obtain matrices with maximum transparency (e.g., 18–20 K for argon and 48–50 K for xenon).

An essential feature of our experimental approach is the use of a fast electron beam to generate radical cations in Freon and solid rare gas matrices. Gamma-ray irradiation is often used in experiments with frozen Freon solutions in glass ampoules. However, this method is not suitable for the experiments with our cryostat; in general, we needed a source of local irradiation with high effici-
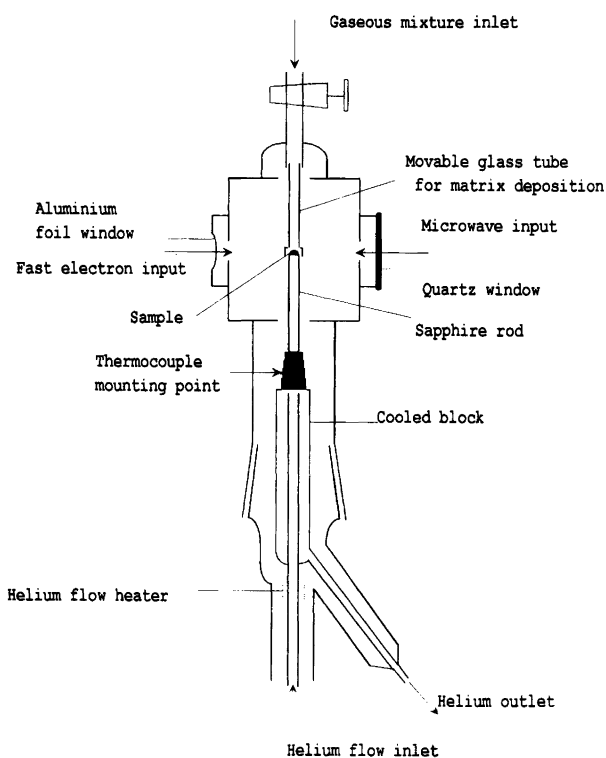
ency. The Bally group used an X-ray radiation source for optical spectroscopic studies of the radical cations generated in an argon matrix.[8,26,27] The limitation of this irradiation method is the low dose rate. Indeed, using X-rays may require several hours of irradiation to generate the concentration of species sufficient for IR spectroscopic studies. An IR cryostat with a built-in electron source (25 keV) has been described by Pacansky and Maier;[30] this complex device was constructed for the studies of radiation-induced effects in very thin deposited layers and polymeric films at cryogenic temperatures. In our experiments we used an EG–2.5 commercial Van-de-Graaf type accelerator for the irradiation of the deposited samples in all the cryostats described. The beam energy was typically ca. 1 MeV. The irradiation doses applied were within the range 10–300 kGy; the maximum irradiation time did not exceed 40 min. Other details of the cryostats used and experimental procedure are given elsewhere.[31–33]

Studies of the formation and properties of radical cations in Freon matrices

The use of combined IR and EPR spectroscopy was tested first for the studies of the radical cations of linear alkenes in Freon matrices at 77 K.[20,34] The radical cations of simple alkenes were among the first species characterized by EPR in frozen Freon solutions.[35] Species of this kind appear to be important intermediates in the radi-

ation-induced polymerization and radiation chemistry of polymers. Alkene molecules form weak specific associates due to π–π interactions. On the other hand, 1-butene, pentenes and higher linear alkenes can exist as different conformers due to rotation of methylene groups adjacent to the double bond. The matrix environment may affect both association and molecule conformation. The questions were whether these effects could be detected by IR spectroscopy in Freon matrices and would there be their any correlations with the trapping and properties of the radical cations as evidenced by EPR spectroscopy? In addition, we intended to look for possible manifestations of the radical cations in the IR spectra.

(E)-2-Butene[20] and a series of (E)-octenes [34] in a $CFCl_3$ (Freon-11) matrix were studied in detail. The state of the parent molecules was monitored by analysing the structure of the strong characteristic band due to out-of-plane C–H bending at double bond, which appears in the region 990–960 cm^{-1}. This intense absorption is a common feature of the IR spectra of E-alkenes. The position of the maximum of this band is known to be sensitive to electrostatic interactions[36] and to conformational changes.[37]

Our studies provided clear evidence for a rather strong interaction between the alkene molecules and the Freon matrix. Indeed, in all cases the maxima of the bands ascribed to isolated alkene molecules in Freon show significant high-frequency shifts in comparison with those for neat glassy alkenes (967–970 cm^{-1} at 77 K).[37] Such behaviour is characteristic of local electrostatic effects reducing the π-electron density of double bonds; in particular, similar shifts were observed for the complexes of olefins with HCl.[36] In most cases, the IR bands under consideration are complex in structure. The interpretation of this structure was based on an analysis of the positions of the component maxima, the concentration dependence of the IR spectrum (the mole ratio of alkene to Freon varied from 400:1 to 20:1) and irradiation behaviour. Figs. 5 and 6 give two illustrative examples. In the case of (E)-2-octene (Fig. 5), the high-frequency component at 973 cm^{-1} [very close to that of (E)-2-butene in Freon-11 [20]] was ascribed to isolated alkene molecules, the feature at 970 cm^{-1} indicated the presence of dimers, and the low-frequency component at 967 cm^{-1} was assigned to larger aggregates. The position of the last-mentioned component coincides with the corresponding band maximum in glassy octene. This assignment is consistent with the observed effect of octene concentration on the IR spectrum.[34] It should be noted that the components of the band considered exhibit different behaviour on irradiation (Fig. 5). The high-frequency component ascribed to monomer alkene molecules shows the most prominent decrease in intensity upon irradiation, whereas the intensity of the low-frequency component does not change significantly. This result implies that the isolated monomer octene molecules participate to a large extent in charge transfer in the Freon matrix. Dimers also undergo some conversion,
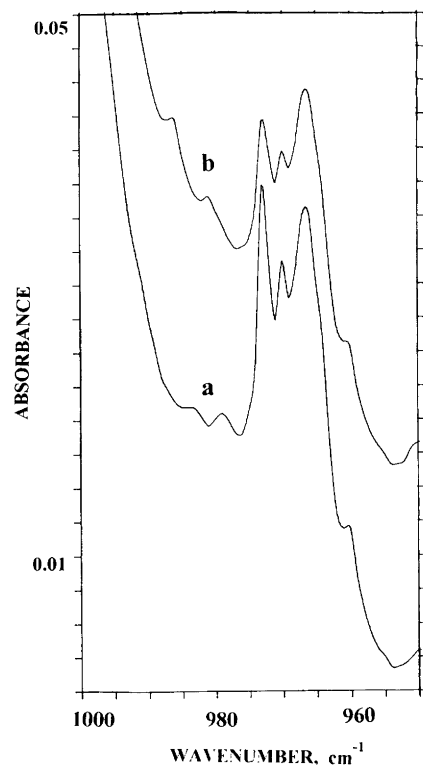

Fig. 5. Fragment of the IR spectrum of deposited mixture of Freon-11 and (E)-2-octene (100:1) taken at 77 K (a) before irradiation and (b) after irradiation up to a dose of 150 kGy.
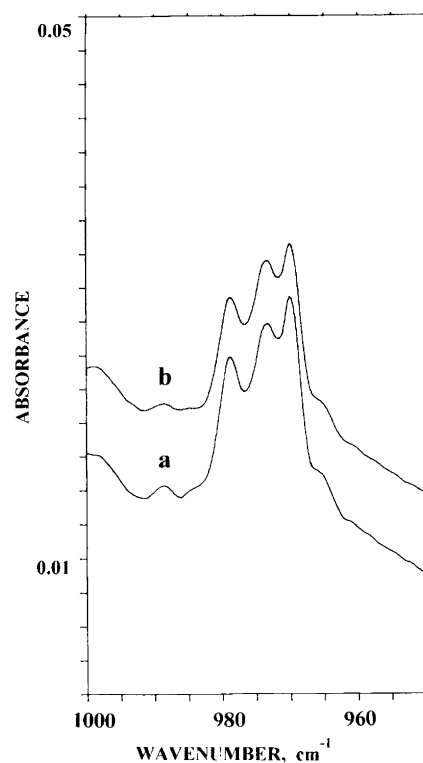

Fig. 6. Fragment of the IR spectrum of a deposited mixture of Freon-11 and (E)-3-octene (100:1) taken at 77 K (a) before irradiation and (b) after irradiation up to a dose of 100 kGy.

whereas larger aggregates are affected to only a small extent. This is just what would be expected for microphase separation.

(E)-3-octene [as well as (E)-4-octene] shows another pattern, which is presented in Fig. 6. In this case, all the components of band structure are shifted toward higher wavenumber in comparison with the band maximum position for neat glassy alkene. Thus, none of these components can be ascribed to large aggregates (microphases). Changes in octene concentration have virtually no effect on the shape of the complex band (relative intensities of the components).[34] The intensity of the band decreases uniformly as a result of irradiation of the sample, i.e., the band components are used with roughly equal efficiency. These observations led us to conclude[34] that the components of the band structure should be ascribed to various conformers of (E)-3-octene monomer molecules trapped in Freon rather than to associates. The conformational nature of the band splitting is supported somewhat by the results of the spectroscopic studies in an argon matrix.[32]

The results of the studies of IR spectra of E-alkenes in Freon-11 are summarized in Table 1. The observed difference between (E)-2-octene and other isomers [(E)-3-octene and (E)-4-octene] can be explained by steric factors, which may control dimerization of alkene molecules. An interesting observation is the unexpectedly large high-frequency shift of some components in comparison with the maxima positions for the corresponding neat alkenes [up to 20 cm⁻¹ in the case of (E)-4-octene]. This result can be interpreted as an evidence of strong interaction of Freon molecules with some specific conformers.

Irradiation of all the systems studied results in the formation of the radical cations observed by EPR spectroscopy. The EPR spectrum of (E)-2-butene radical cation observed in our studies[20] was essentially the same as that reported in Ref. 35. The interpretation of the spectra of octene radical cations in Freon matrices is discussed in Refs. 19, 34 and 38. Formation of alkyl-type radicals was observed at high concentrations of (E)-2-octene in Freon-11;[34] only one conformer of the radical cation was identified in dilute solutions of this alkene in various Freons.[19,34,38] The presence of several conformers of the radical cations has been suggested for (E)-3-octene and (E)-4-octene;[34] however, poor spectral resolution prevented us from making a definite identification of the conformers.

An intriguing question is concerned with the presence of new bands in the IR spectra, which could be assigned to alkene radical cations. In the studies of (E)-2-butene,[20] we observed only one rather intense feature at ca. 1135 cm⁻¹ that did not appear upon irradiation of neat butene or Freon. The annealing behaviour of this band was similar to that of the radical cation observed by EPR. Similar bands have been observed in the IR spectra of irradiated (E)-octenes in Freon-11.[34] We assumed tentatively that this absorption may be due to out-of-plane C–H bending at the ionized double bond in the radical cations. This implies that ionization results in a large high-frequency shift of this band (by ca. 160 cm⁻¹) and in growth of its intensity. From a qualitative point of view, one may expect such a frequency shift extrapolating the effect of reduction of π-electron density of the double bond on the vibration under consideration (see

Table 1. Structure of the IR absorption bands due to out-of-plane bending in E-alkenes in a Freon-11 matrix at 77 K.

Alkene	Maximum position, cm⁻¹	Assignment	EPR results for irradiated system	Ref.
(E)-2-butene	975	Monomer	Monomeric radical cation	20
	967	Aggregates		
(E)-2-octene	973	Monomer	Monomeric radical cation;	34
	970	Dimer	Dimeric radical cation and alkyl	
	967	Aggregates	Radical at high concentration	
(E)-3-octene	979	Various conformers	Radical cations[a]	34
	974	of monomer molecules		
	970			
(E)-4-octene	990	Various conformers	Radical cations[a]	34
	985	of monomer molecules		
	977			

[a] The EPR spectrum is poorly resolved (probably a mixture of conformers).

above). In general, both theoretical and experimental studies [24, 25, 39] have demonstrated the possibility of very large effects of ionization on the intensities of some IR absorptions in aromatic systems. However, no theoretical or experimental studies have been reported for linear alkenes. Thus, the identification of the observed band is still tentative, taking into account the complicated nature of radiation-induced processes in the systems under consideration.

The results of the studies of alkenes in Freon matrices show that IR spectroscopy may provide valuable information about the state of the parent molecules in the matrix, which is helpful for an analysis of the formation and properties of radical cations. In addition, one may hope to obtain signs of the IR absorptions of radical cations (although their interpretation is not straightforward). The limitations of using Freon matrices for combined spectroscopic studies are obvious. First, these matrices show rather strong interaction with parent molecules and radical cations that may have a considerable effect on both IR and EPR spectra. Second, Freons exhibit several very strong absorptions below 1500 cm^{-1}, so rather large regions of the IR spectrum are not transparent in Freon matrices. For this reason, some characteristic absorptions of radical cations and radiolysis products could not be detected in Freon matrices. Thus, for basic spectroscopic and radiation-chemical studies it is important to extend the approach used to inert and transparent media, i.e., to solid rare gas matrices.

Studies of radiation-induced behaviour of hydrocarbon molecules in solid rare gas matrices

Organic radical cations generated by ionizing radiation can be trapped in solid rare gas matrices doped with electron scavengers. The proper choice of matrix gas is of primary importance in this case. This point should be considered taking into account both spectroscopic and energetic criteria.

Solid neon appears to be an ideal matrix material from a spectroscopic point of view since it has the lowest polarizability. It is expected that using a neon matrix one can observe non-perturbed spectra of the radical cations. However, this matrix has very narrow range of thermal stability, which causes serious technical problems. Argon is the most popular matrix material (especially for optical spectroscopic studies). It is more polarizable than neon; nevertheless, the 'electronic rigidity' of argon is also sufficiently high. Xenon has a far more 'soft' (distortable) electronic shell than argon, so interactions with the xenon matrix may affect the electronic structure and spectra of the radical cations to a certain extent.

The significance of energetic criteria (ionization potential of matrix molecules) results from the mechanism of generation of solute radical cations in radiation-

chemical experiments.[8] The energy of ionizing radiation is absorbed primarily by the matrix, and formation of the radical cations of isolated organic molecules is due to positive hole transfer (indirect ionization). This process is highly exothermic in neon and argon matrices. Indeed, the gas phase ionization potentials (IP) of neon and argon are 21.56 and 15.75 eV, respectively, whereas IP values of organic molecules are typically close to 10 eV.[40] These very large IP 'gaps' (i.e., excess energy in hole transfer processes) should result in the formation of organic radical cations in excited states, which may undergo rapid fragmentation or rearrangements (an example is given in Ref. 41). The probability of these rapid chemical transformations occurring in neon and argon matrices is high because the excess energy dissipation due to phonon–lattice modes is inefficient. As a result, a neon matrix appears to be unsuitable for the radiolytic generation of the radical cations. The possibility of trapping of primary radical cations in argon should be determined essentially by the efficiency of internal conversion of excess energy in the cation. In contrast, xenon has considerably lower IP (12.13 eV;[40] this value is close to those of Freons). Thus, in the case of xenon, the IP 'gaps' are smaller, so one can expect formation of the ground-state solute radical cations. This implies that xenon is probably the best choice from an energetic point of view. On the other hand, comparative studies using argon and xenon matrices may provide direct information about the effect of excess energy on trapping and properties of the radical cations.

Recently we began systematic studies of the formation and reactions of aliphatic radical cations in xenon and argon matrices using a combination of IR and EPR spectroscopy. At first, we focused our attention on linear alkanes. The main purposes of these studies were as follows: (i) to test the conditions for trapping of the primary radical cations in solid rare gas matrices; (ii) to examine the products of degradation of excited alkane radical cations in these matrices; (iii) to make an attempt to identify the IR spectra of the radical cations. Several alkanes were examined; however, systematic quantitative data were obtained mainly for heptane.
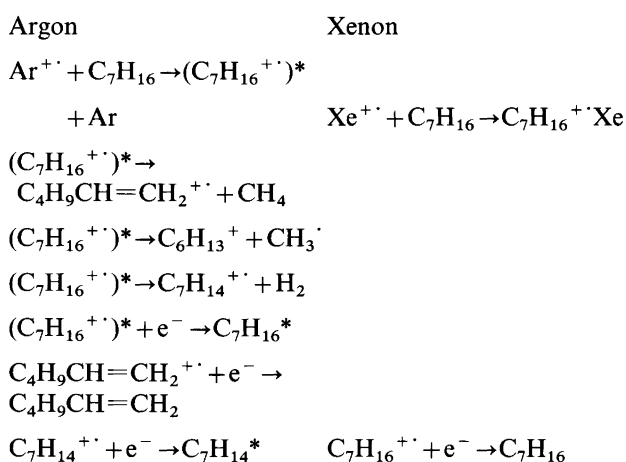
As a first step, we analysed the radiation-induced degradation of heptane molecules in argon and xenon without electron scavengers by IR spectroscopy.[42,43] It was found that alkane molecules underwent very efficient degradation upon electron-irradiation in both argon and xenon matrices at 15 K. The lower limit of the yield of consumption of heptane molecules in argon $G(-C_7H_{16})$ was estimated to be at least 1.4 molecule/100 eV from IR spectroscopic data (mole ratio of argon to heptane 500:1).[42,43] The corresponding yield, formally calculated per unit energy absorbed directly by heptane molecules is at least 230 molecule/100 eV. This result implies high efficiency of positive hole and/or excitation transfer in argon. Qualitatively similar results were obtained for heptane and pentane in a xenon matrix. It should be noted that the yields of radiation-induced degradation

of alkane molecules in solid rare gas matrices obtained in our work are several times higher than the yields of free radicals measured in the EPR studies of alkane radiolysis in argon, krypton and xenon at 4.2 K.[44] This difference may indicate the significance of non-radical pathways of alkane molecule degradation.

The main products of heptane degradation in argon and xenon identified by IR spectroscopy at 15 K are methane, vinyl and *trans*-vinylene olefins, and allyl-type radicals; a detailed analysis is presented in Refs. 42 and 43. The nature of matrix strongly affects the relative abundance of these products; in particular, the yields of methane and vinyl olefins are higher in argon, whereas *trans*-vinylene olefins predominate in xenon. This result led us to conclude that C–C bond rupture was favoured in an argon matrix. Such behaviour is ascribed to the fragmentation of excited heptane radical cations resulting from highly exothermic positive hole transfer from argon to heptane.[42,43] On the other hand, radiolysis products observed in a xenon matrix appear to result from excited alkane molecules rather from radical cation. The following scheme of basic radiation-induced transformations of heptane molecules in argon and xenon has been proposed.[43]
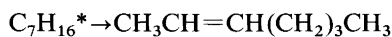
$$M \rightarrow M^{+\cdot}, e^-, M^* \ (M = Ar, Xe)$$

Ionic reactions:

Argon   Xenon

$$Ar^{+\cdot} + C_7H_{16} \rightarrow (C_7H_{16}^{+\cdot})^*$$

$$+ Ar \qquad\qquad Xe^{+\cdot} + C_7H_{16} \rightarrow C_7H_{16}^{+\cdot} Xe$$

$$(C_7H_{16}^{+\cdot})^* \rightarrow$$
$$C_4H_9CH=CH_2^{+\cdot} + CH_4$$

$$(C_7H_{16}^{+\cdot})^* \rightarrow C_6H_{13}^+ + CH_3^\cdot$$

$$(C_7H_{16}^{+\cdot})^* \rightarrow C_7H_{14}^{+\cdot} + H_2$$

$$(C_7H_{16}^{+\cdot})^* + e^- \rightarrow C_7H_{16}^*$$

$$C_4H_9CH=CH_2^{+\cdot} + e^- \rightarrow$$
$$C_4H_9CH=CH_2$$

$$C_7H_{14}^{+\cdot} + e^- \rightarrow C_7H_{14}^* \qquad C_7H_{16}^{+\cdot} + e^- \rightarrow C_7H_{16}$$

Reactions of excited molecules:
General

$$C_7H_{16}^* \rightarrow CH_3CH=CH(CH_2)_3CH_3$$

and/or

$$CH_3CH_2CH=CH(CH_2)_2CH_3 + H_2$$

$$C_7H_{16}^* \rightarrow C_4H_9CH=CH_2 + CH_4$$

Argon   Xenon

$$C_7H_{14}^* \rightarrow RCH \overset{-}{-} CH \overset{-}{-} CHR'$$

$$+ H^\cdot \qquad\qquad C_7H_{16}^* \rightarrow C_7H_{15}^\cdot + H^\cdot$$

$$C_4H_9CH=CH_2^* \rightarrow$$
$$C_3H_7CH \overset{-}{-} CH \overset{-}{-} CH_2 + H^\cdot$$
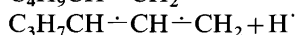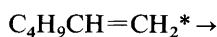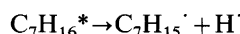
According to this scheme, the basic difference between the processes in argon and xenon results from different electronic states of heptane radical cations formed in the charge-transfer processes in these matrices.

This mechanism can be tested by analysing the effect of electron scavengers on the formation of radiolysis products. The major question is whether the ground-state alkane radical cations can be trapped and identified by EPR and IR spectroscopy in xenon and argon matrices containing electron scavengers. This was the subject of the most recent investigations. In our studies we used mainly $CFCl_2CF_2Cl$ (Freon-113) as an electron scavenger. The reasons for this choice were as follows: (i) as was mentioned above, Freons are ideally suited to EPR studies since the radicals resulting from these scavengers give typically broad and very weak EPR spectra in glasses and polycrystals; (ii) Freons do not have light hydrogen atoms, so both Freons and the products of their transformations cannot exhibit any absorptions in the high-frequency region of IR spectrum, which may facilitate identification; (iii) specifically, Freon-113 has a high IP value (11.99 eV), which is very close to that of xenon and it is expected that this scavenger will not compete with alkanes for matrix positive holes (at least, in xenon).

Fig. 7 shows the central part of the EPR spectrum of the system xenon–heptane–Freon-113 irradiated at 15 K. This spectrum exhibits a broad triplet with a splitting of ca. 31 G, which is very close to hyperfine splitting in heptane radical cation observed in Freon matrices.[45,46] Thus, the identification of the spectrum appears to be quite straightforward. It should be noted that only trace amounts of trapped hydrogen atoms (doublet with characteristic separation of about 500 G and satellite lines due to interaction with Xe magnetic nuclei) are observed in the system under consideration. In contrast with this result, trapped hydrogen atoms and alkyl radicals are the major paramagnetic products of the radiolysis of heptane in xenon containing no electron scavenger under the same conditions (short alkanes irradiated in xenon at 4.2 K show similar behaviour[44]). Such an effect of Freon-113 on the formation of paramagnetic species appears to be in good accord with the radiolysis scheme presented above. Indeed, hydrogen atoms and heptyl radicals are thought to result from homolytic cleavage
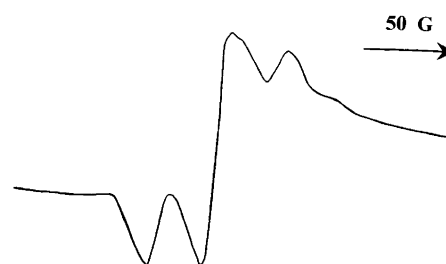

50 G

Fig. 7. EPR spectrum of the deposited mixture xenon–heptane–Freon-113 (400:1:2) irradiated with fast electrons (40 kGy) at 15 K.

of C–H bonds in excited neutral heptane molecules, which are produced mainly in the process of ion–electron recombination. Acting as an electron scavenger, Freon-113 prevents recombination thus reducing the yield of H atoms and neutral radicals. At the same time, the primary radical cations are trapped in the xenon matrix.

In the case of argon matrix doped with Freon-113, the situation is quite different. Fig. 8 shows the central part of the EPR spectrum of irradiated mixture argon–heptane–Freon-113. In this spectrum one can see a sharp quartet with a splitting of 23 G superimposed on a broader spectrum probably consisting of an even number of lines. The quartet spectrum is characteristic of the methyl radical. It is interesting to note that the intensity ratio in this quartet appears to be neither 1:3:3:1 (classic binomial) nor 1:1:1:1 (characteristic of the lowest rotational state observed at 4.2 K [44]); such an 'intermediate' pattern is caused by the measurement temperature used in our experiments. The broad multiplet cannot be assigned definitely from the present data. This spectrum may be due to an alkyl radical (either heptyl or shorter); however, the presence of other kinds of paramagnetic species cannot be excluded. Anyway, no evidence of trapping of primary heptane radical cations in argon was obtained. In addition to the signal shown in Fig. 8, a doublet from hydrogen atoms with a splitting of 510 G is observed in an argon matrix. The lines of this doublet are very sharp and well defined; however, their integrated intensity is low in comparison with that of the central signal. Hydrogen atoms and methyl radicals were detected previously in irradiated argon–propane and argon–isobutane mixtures at 4.2 K.

The IR spectra of irradiated mixtures xenon–heptane–Freon-113 and argon–heptane–Freon-113 show considerable degradation of the parent alkane molecules upon irradiation (similar to the case of the systems containing no electron scavenger). Nevertheless, the presence of the scavenger has a remarkable effect on the formation of the radiolysis products. This effect is matrix-dependent, i.e., Freon-113 affects the product yields differently in argon and xenon matrices. In particular, methane forma-

tion (monitored by the relative intensity of the characteristic band at ca. 1300 cm^{-1}) in xenon is suppressed by a factor of ca. 5 in the presence of Freon-113. On the other hand, methane formation in argon is affected only slightly by addition of Freon-113 (reduction by ca. 25%). This observation indicates different mechanisms of methane formation in these two matrices, which is in general accordance with the scheme proposed above. Indeed, in the case of xenon matrix, methane appears to result mainly from neutral excited heptane molecules. As was stated above, the yield of these precursors should decrease in the presence of Freon-113 because of the decreased probability of ion–electron recombination. In an argon matrix, methane is formed mainly as a result of fragmentation of excited heptane cations, which occurs in the presence of Freon-113 as well. Thus, rapid fragmentation of excited alkane radical cations may compete with the ion–electron neutralization in an argon matrix. Two fragmentation pathways can be deduced from the present data, one yielding methyl radical and hexyl cation (from EPR results), and the other yielding methane and 1-hexene radical cation (indicated by IR spectroscopic results). Unfortunately, the EPR spectrum obtained in an argon matrix (Fig. 8) does not allow us to conclude firmly whether 1-hexene radical cation is trapped or not in the system under study.

The effect of Freon-113 on the formation of olefinic products of heptane radiolysis in argon and xenon matrices cannot be easily monitored quantitatively because of essential changes of bandshape and maximum positions in the presence of Freon. In part, this may be due to overlapping with the bands of Freon radiolysis products; also some kinds of interaction may affect the IR bands of π-systems in the irradiated systems under consideration. In addition to heptane radiolysis products, several rather strong bands were shown to result from Freon radiolysis in the systems studied. In a xenon matrix, the most intense absorptions due to products from Freon appear at 1794, 1325, 1198 and 1070 cm^{-1}; these bands are also observed in the irradiated xenon–Freon systems containing no alkanes.

Since we have found that heptane radical cations are generated radiolytically and trapped in a xenon matrix doped with Freon-113, it is logical to try to find features in the IR spectrum of the same system that can be ascribed to the radical cations. Fig. 9 demonstrates the effect of irradiation on the high-frequency region of the IR spectra of this system. As was stated above, this spectral region cannot be affected by any bands from Freon radiolysis products. The main new feature of the spectrum presented is the broad absorption with the maximum positioned at ca. 2770 cm^{-1} (the formation of this band in the presence of electron scavengers was first marked in our earlier work,[42,43] before the EPR data confirming the trapping of the radical cations were obtained). This absorption appears in the region characteristic of 'unusual' C–H stretchings; on the other hand, it is not observed in the irradiated xenon–heptane system
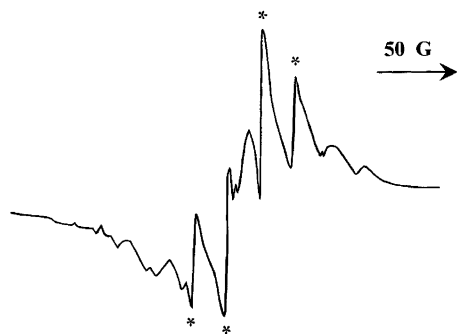

Fig. 8. EPR spectrum of the deposited mixture argon–heptane–Freon-113 (400:1:2) irradiated with fast electrons (50 kGy) at 15 K. The signals from methyl radicals are marked with asterisks.
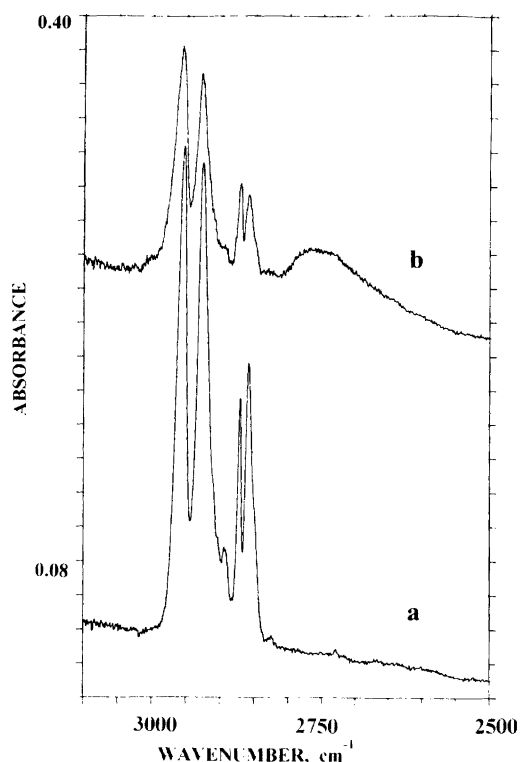
Fig. 9. Fragment of the IR spectrum of the deposited mixture xenon–heptane–Freon (400:1:2) taken at 16 K (a) before irradiation and (b) after irradiation with fast electrons (270 kGy).

Fig. 10. Fragment of the IR spectrum of the deposited mixture argon–heptane–Freon (400:1:2) taken at 16 K (a) before irradiation and (b) after irradiation with fast electrons (220 kGy).

without electron scavengers. The band was ascribed tentatively to C–H stretchings in heptane radical cation;[42,43] this assumption is in accord with annealing behaviour of the system monitored by comparison of EPR and IR spectra. The EPR spectrum of the radical cation decays essentially at ca. 90 K; the IR band at 2770 cm^{-1} shows some changes in the shape and observed maximum position at 40–80 K (probably, due to local matrix relaxation) and also decays sharply at 90 K. We failed to observe any products of the thermal decay of the radical cations (such as alkyl radicals, which could result from an ion–molecule reaction) by EPR or IR spectroscopy. This may be due to matrix instability at 90–100 K, which makes it nearly impossible to differentiate primary and secondary reactions.*

Qualitatively similar absorptions at ca. 2770 cm^{-1} were observed with other linear alkanes and with CCl_4 as an electron scavenger in a xenon matrix. On the other hand, irradiation of heptane in argon in the presence of Freon-113 does not result in the appearance of an absorption of this kind (Fig. 10); this result is in accordance with the EPR data, which reveal no trapped heptane radical cations in an argon matrix.

It is clear that the data obtained give only an indication of the vibrational features of the radical cation. This

* Note that xenon shows appreciable pressure at these temperatures, and the conditions of our studies are quite different from those of 'ampoule' experiments.[9]
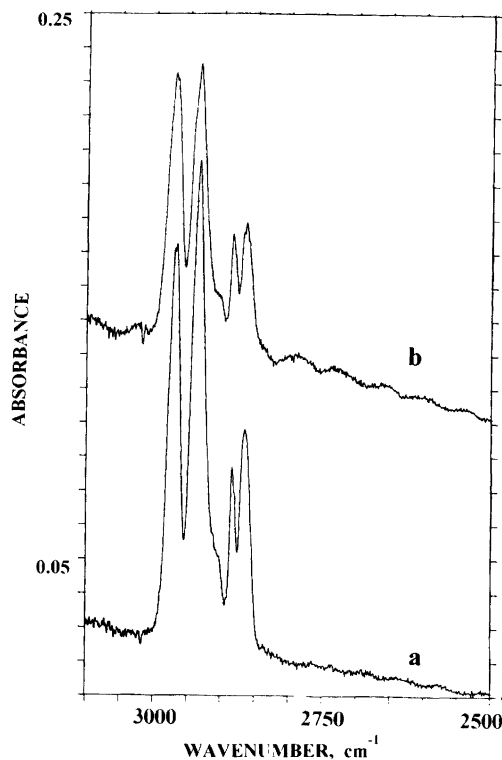
result alone does not allow us to make reliably correct assignments and analysis of the effects of ionization on molecular vibrations. Ideally, one should have experimental features, which respond to most fundamentals (as has been demonstrated in some comprehensive experimental and theoretical studies of ionized conjugated dienes [26,27]). Unfortunately, up to now, we have failed to observe any other features in the IR spectrum that could definitely be ascribed to heptane radical cations, in spite of high conversion of the parent heptane molecules. One possible explanation is that these absorptions may be broad and weak due to strong cation–matrix interactions (note that the band at ca. 2770 cm^{-1} is also very broad). As a merely qualitative speculation, one may assume that large low-frequency shifts of the C–H stretchings in the radical cation (in comparison with those in parent neutral molecule) result from selective weakening of some specific C–H bonds in the radical cations, which is consistent with the EPR results on selective deprotonation of ionized linear alkanes.[15–18] In this case, the IR spectroscopic information (even very limited) could be considered as a very important test. However, the polarization of xenon matrix may have strong effect on the magnitude of the observed shift, so the broad absorption detected may belong rather to a 'bunch' of C–H stretchings in the charged species (radical cation) than to any specific feature.

Evidently, we are at the very start of systematic

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combined spectroscopic studies of the radical cations in solid rare gas matrices. At present, we are able to discriminate between trapping of ground-state radical cations and the formation of products of fragmentation of excited cations. To obtain more information from IR spectra, we need to find a compromise between the energetic and spectroscopic criteria described above. One way to approach this problem is to vary the matrix composition (i.e., to use krypton or solid rare gas mixtures instead of xenon). Studies in this direction are in progress now.

Concluding remarks

The experimental approach to the studies of matrix isolated radical cations using a combination of EPR and IR spectroscopy opens new possibilities for obtaining information about trapping, structure and properties of reactive radical cations in various matrices. Both techniques are informative from a structural point of view and sensitive to rather 'subtle' effects. One version of the approach used relates to the studies of the radical cations in Freon matrix samples prepared by the matrix deposition technique at 77 K. It should be noted that application of this procedure instead of the widely used frozen solution technique may provide a key to understanding of some puzzling matrix effects observed in earlier studies. IR spectroscopic data give essential information about matrix–solute and solute–solute interactions prior to ionization. These interactions may be strong, especially for molecules containing polarizable π-bonds; they are likely to affect trapping and properties of the radical cation formed upon ionization.

Studies of the radiolytically produced radical cations in solid rare gas matrices by combination of EPR and IR spectroscopy can provide basic spectroscopic information concerning the structure of the radical cations in ground and excited states. The matrix IP has a considerable effect on the trapping of radical cations. The results obtained show that linear alkane radical cations cannot be prepared by radiolytic generation in an argon matrix because of rapid fragmentation of excited species resulting from positive hole transfer in argon. This is probably also the case for other systems, which cannot dissipate excess energy in some physical processes. The success of the Bally group in preparing the radical cations of some conjugated dienes in argon by X-irradiation[26,27] may be due to high efficiency of internal relaxation of excess energy without chemical transformations in these cations. More work needs to be done to clarify the criteria of stability of the radical cations in argon.

Use of xenon doped with electron scavengers as a matrix material appears to be a more common way of obtaining trapped radical cations, although experimental evidence is still very limited. In this case, the main disadvantage results from the high polarizability of xenon, which may have a strong effect on the IR absorptions of the radical cations. Generally speaking, the effect

of polarization of xenon on specific absorptions should correlate with the charge distribution in the radical cation. In particular, a large and uniform effect can be expected for σ-delocalized linear alkane radical cations with charge distributed over molecular skeleton. On the other hand, the situation may be essentially different for systems with a localized cationic centre, where only some absorptions should be affected significantly by matrix interaction. From this point of view, the case of distonic radical cations with spatial separation of radical and cationic sites is of special interest.

An interesting aspect of comparative studies of radiation-induced processes in solid rare gas matrices with various IP is concerned with the possibility of obtaining experimental information about the chemical properties of excited radical cations in the condensed phase. Analysis of both paramagnetic and diamagnetic products of cation reactions in an argon matrix by EPR and IR spectroscopy makes it possible to establish the reaction mechanism. In particular, in the case of heptane, both EPR and IR spectroscopic data provide evidence for the preferential cleavage of the $C(1)$–$C(2)$ bond in the excited radical cation. This result is inconsistent with the data of photochemical studies in Freon matrices [47,48] that revealed the formation of mainly butene radical cation from photo-excited heptane radical cation. For this reason, it would be of interest to compare the products of photochemical reactions of the radical cations in xenon with the products directly resulting from the same parent molecules in argon.

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