

Review Article

Asymmetric Distortion of Alkane Radical Cations as Studied by EPR Spectroscopy: the Role of Pseudo-Jahn–Teller Effects and Matrix Interactions†

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In a series of recent works we have shown that the radical cations of several alkanes, such as propane, norbornane, *n*-pentane, and its methyl-substituted derivatives, which do not have degenerate HOMOs, are distorted in several matrices at low temperatures. These cations distort in a direction unique to each system regardless of the matrix employed, but the extent of deformation is dependent on the matrix. The two equivalent distorted structures are dynamically averaged at elevated temperatures. From these observations, the mechanism of the distortion was attributed to a pseudo-Jahn–Teller (JT) effect assisted by matrix interactions. The distortion of ethylene cation recently observed by EPR spectroscopy is rationalised in the same way. This paper is a review of our studies of the title phenomenon.

Since the EPR spectral detection of the ethane radical cation by means of the matrix isolation technique,¹ the electronic as well as the geometrical structures of the radical cations of many simple alkanes have been clarified.^{2–5} An important result is the direct observation of the Jahn–Teller (JT) distortion of these compounds. Although the role of matrix interactions in the stabilization of the distorted form cannot be neglected and is referred to as ‘matrix assisted JT distortion’, the direction of distortion is determined by the intrinsic nature of the molecule.⁶ On the other hand, EPR spectra of the radical cations of most alkanes having no degenerate highest occupied molecular orbitals (HOMO) have been successfully analyzed on the assumption that the symmetry of the mother molecule is maintained after ionization. However, Shiotani, Lindgren and their coworkers have reported that the radical cations of methylcyclohexane and some related compounds in haloalkane matrices have distorted structures with one especially elongated C–C bond.^{7–9} They considered this result as a JT distortion of the cyclohexane cation, and the methyl group as a perturbation which removes the degeneracy of the HOMOs. Contrary to this, it was pointed out that a

substituted alkyl group makes an important contribution to the HOMO in a σ -electron system, and thus this system should be considered as a branched alkane,¹⁰ in which the unpaired electron tends to localize in the proximity of the tertiary carbon.¹¹ Shortly after that, we observed an asymmetrically distorted propane cation in a perfluoropropane matrix.^{12,13} At first, we considered the distortion to be inherent to the propane radical cation, since the matrix used, C₃F₈, is expected to supply a sufficiently large substitutional trapping site for the propane cation. In addition, there had been a few theoretical predictions that the propane cation in the ground state has an asymmetric structure.^{14,15} Therefore, we extended our studies to find other distorted non-JT cations in order to elucidate the mechanism of this phenomenon. We were able actually to observe evidence of distortion for the cations of *n*-pentane and its methyl-substituted derivatives with C_{2v} symmetry (*trans*–*trans* conformers),¹⁶ and norbornane.¹⁷ In these studies it was found that the degree of distortion of the cations and their dynamics are strongly dependent on the matrix, although its direction is unique to each system regardless of the matrix. As a result, we reached the conclusion that distortion in these systems can be understood by the concept of the so-called ‘pseudo-JT effect’.^{18–20}

In this report, we summarize a series of our studies on

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the asymmetric distortion of alkane radical cations. The role of the pseudo-JT effect and of matrix interactions in the stabilization of the distorted structures is described. The asymmetric distortion of the radical cation is important since this is a preparative step for the subsequent reaction.²¹⁻²³ Finally, we discuss briefly the distortion of ethylene radical cation, whose EPR spectrum has been observed recently.²⁴

EPR observation of the distorted structure of alkane radical cations

Propane cation. EPR spectra of $C_3H_8^+$ generated by radiolysis at 4 K and observed at 4 K in a variety of matrices are shown in Fig. 1. The bottom two (C in SF_6 and D in $CFCl_3$) were assigned, in previous studies,^{1,25} to the cation with an unpaired electron in $4b_2$ (1) and $2b_1$ (2) of C_{2v} symmetry (inset I), respectively. A large hfc (about 9 mT) of cation 1^+ generated in C_3F_8 is due to the two methyl protons which lie in the molecular plane of the C-C frame. In 2^+ generated in $CFCl_3$, however, a large part of the unpaired electron is delocalized in the pseudo- π orbital and the two methylene protons and four out-of-plane methyl protons have hfc of 10.5 and 5.3 mT, respectively. The fact that propane cation is stabilized with having different singly occupied molecular orbitals (SOMO) in different matrices may be related to the fact that the energies of the three highest occupied MOs ($4b_2$, $2b_1$, $6a_1$) are close to each other in this system.^{26,27}

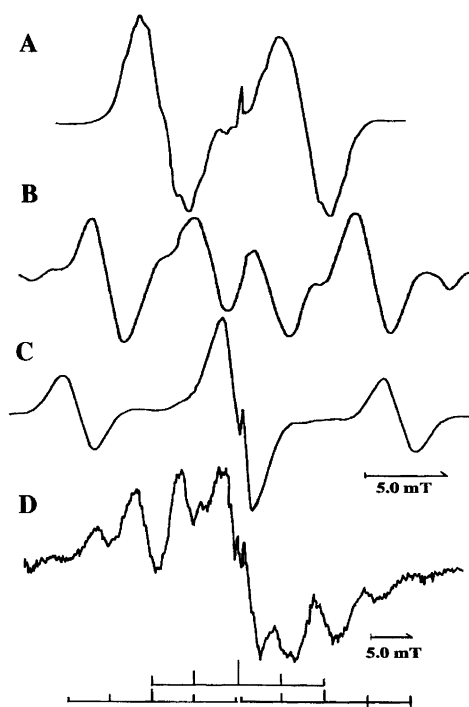
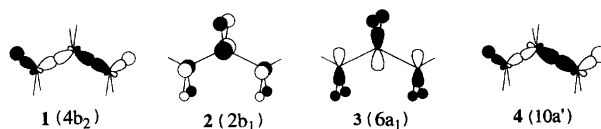


Fig. 1. EPR spectra of propane radical cation generated by X-ray radiolysis at 4 K and observed at the same temperature in: C_3F_8 (A), C_2F_6 (B), SF_6 (C), and $CFCl_3$ (D).



The SOMO of propane cation in C_3F_8 (A) cannot be assigned to 1^+ , 2^+ or 3^+ , since this cation has only one proton with a large hfc of about 9.0 mT. In addition, at temperatures higher than 77 K, spectrum A changes reversibly into three lines with the same spectral width. Thus it was assigned to species 4^+ , where the unpaired electron occupies $10a'$ of C_s symmetry, which is formed from 1^+ by elongation of one of the two C-C bonds.^{12,13} An INDO calculation shown as Fig. 2A assuming a difference of 0.055 nm between the two C-C bonds corroborated the spectrum observed in C_3F_8 . The spectrum observed in C_2F_6 (Fig. 1B) shows four lines due to two non-equivalent protons, and is easily assigned to the radical cation distorted similarly but to a smaller extent than in C_3F_8 . The hfc calculated by the INDO method as functions of the difference between the C-C bond lengths are shown in Fig. 2B. With increased distortion, the hfc of one of the two in-plane methyl protons increases a little initially but then decreases gradually, while the other hfc decreases steeply and monotonously. Therefore, the sum of the two hfc, i.e., the overall width

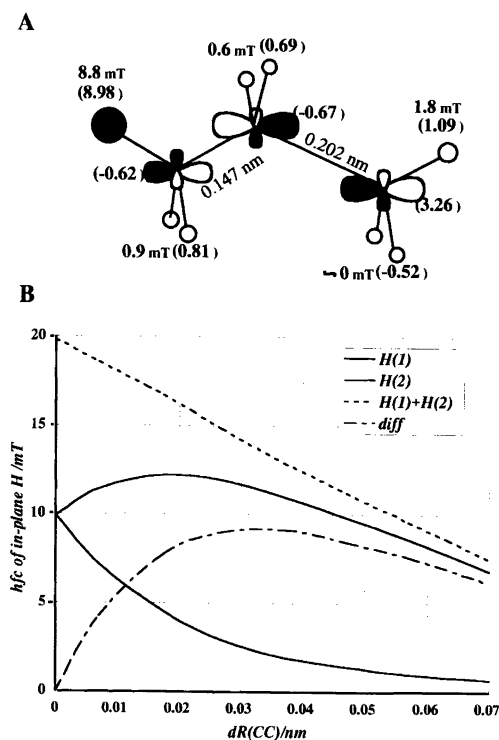
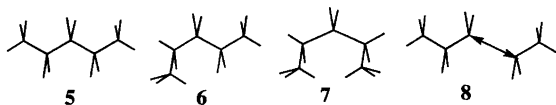


Fig. 2. INDO calculations for propane cation whose unpaired electron occupies the $4b_2$ orbital (C_{2h}) or its modification $10a'$ (C_s): A, the SOMO and the shape of propane cation stabilized in C_3F_8 ; B, calculated hfc of the two methyl protons in the molecular plane (—), and the sum (...) and the difference (— · —) of these, as functions of the difference between the two C-C lengths.

of the spectrum, is a good indicator of the distortion. The difference between the two hfc can also be an indicator, but only when the distortion is not too large.

The temperature dependence of the spectra is shown in Fig. 3 for $\text{CH}_3\text{CD}_2\text{CH}_3^+$ in C_3F_8 . Spectra for the partially deuteriated system are shown, since the resolution is much better than that for the non-labelled system, which also shows the same temperature dependence. The spectral changes at temperatures below 77 K are interpreted as being due to rapid exchange between the two equivalent geometries, one of which is the mirror image of the other. D–F are spectra calculated by use of the modified Bloch equation for two-site jumping. It is notable that (1) these dynamics are partially allowed even at 4 K, and (2) it is more rapid in the system just after the radiolysis at 4 K than after annealing at 77 K. At temperatures higher than 80 K, internal rotation of the methyl group becomes rapid enough to make the six methyl protons equivalent.²⁸

Radical cation of *n*-pentane and methyl-substituted *n*-pentanes. Three types of *n*-pentane radical cation, the *trans*–*trans* conformer (TT: 5^+) with C_{2v} symmetry, the *trans*–*gauche* (TG: 6^+) conformer, and the *gauche*–*gauche*' form (GG': 7^+) have been identified using $\text{CFCl}_2\text{CF}_2\text{Cl}$ (Fig. 4D)^{25,29} and CF_3CCl_3 ^{30,31} as the matrix.



In addition to these, an asymmetrically distorted *n*-pentane cation with TT conformation (TT: 8^+) was found in SF_6 at 4 K (Fig. 4A).¹⁶ At 77 K, the spectrum

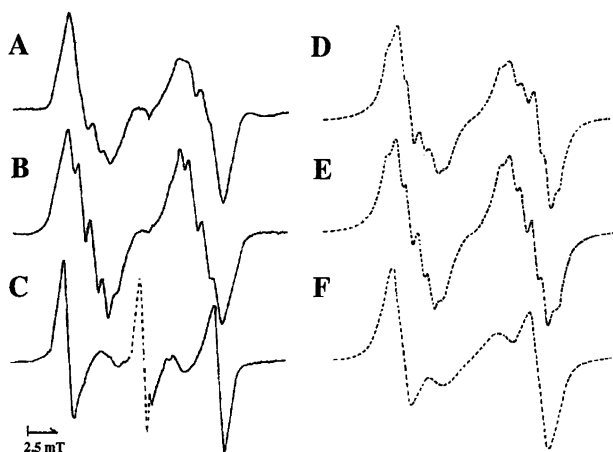


Fig. 3. Temperature dependence of the EPR spectra of partially deuteriated propane cations ($\text{CH}_3\text{CD}_2\text{CH}_3^+$) in C_3F_8 , and their simulations. Observations were made at 4 K after radiolysis (A), at 4 K after annealing at 77 K (B), and at 77 K (C). D, E and F are simulations using the modified Bloch method for the two-site exchange process at correlation times of 2.5×10^{-8} s, 7.5×10^{-8} s, and 7.5×10^{-9} s, respectively.

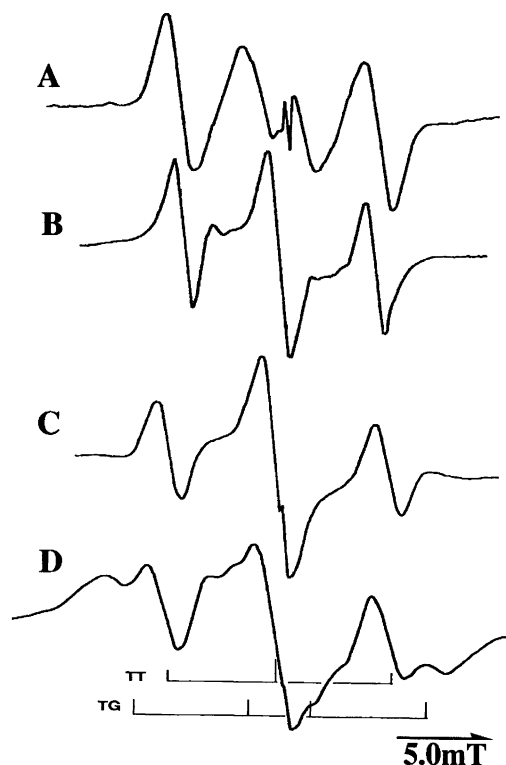
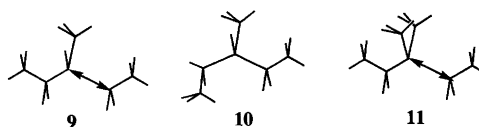


Fig. 4. EPR spectra of *n*-pentane radical cation generated in SF_6 (A, B), $n\text{-C}_6\text{F}_{14}$ (C), and $\text{CFCl}_2\text{CF}_2\text{Cl}$ (D) by X-ray radiolysis at 4 K. Observations were made at 4 K (A, C) or 77 K (B, D).

changes into three lines (Fig. 4B) with the same overall width due to the exchange process between the two equivalent distorted forms. On the other hand, the cation formed in $n\text{-C}_6\text{F}_{14}$ (Fig. 4C) keeps the C_{2v} symmetry [5^+ : $a(\text{H}^{11}) = a(\text{H}^{51}) = 5.5$ mT], and shows no appreciable spectral change in the temperature range 4–77 K. In addition to the temperature dependence, 5^+ and 8^+ are distinguishable by the fact that the spectral width of 5^+ is larger than that of 8^+ . As is the case for propane cation, INDO calculations indicate that the sum of the two main proton hfc decreases with increased distortion. The distorted TT cation 8^+ can be distinguished from the TG conformer 6^+ , which also shows two different proton hfc, by the following facts: (1) the two proton hfc of the TG conformer are known to be larger than those for the undistorted TT by about 40%,^{25,30,31} and (2) the reversible spectral change at temperatures 4 and 77 K can hardly be expected for the TG conformer, since internal rotation of the ethyl group is difficult at such a low temperature. The hfc observed in SF_6 were obtained by INDO calculation with the assumption that $\text{C}_2\text{--C}_3$ is elongated by 0.005 nm and $\text{C}_3\text{--C}_5$ is shortened by the same length.



A radical cation with an asymmetrically distorted TT conformation was also detected for 3-methylpentane (9^+) and 3,3-dimethylpentane (11^+) in C_8F_{18} and perfluoromethylcyclohexane, respectively.¹⁶ A large part of cation 9^+ disappeared upon warming the sample at 77 K with an accompanying increase of the TG conformer (10^+) probably by hole transfer. Thus, the dynamics of this cation could not be investigated. The distorted 3,3-dimethylpentane 11^+ was stable and rigid even at 77 K.

Norbornane cation. Fig. 5 shows the EPR spectra of norbornane cation generated in several matrices at 4 K. In a previous study, norbornane cation was detected in $CFCl_2CF_2Cl$ (C) and the electronic structure was assigned to 2A_2 , where the hf structure of 6.5 mT is assigned to the four *exo*-protons.^{32,33} We found that the radical cation shows a similar five-line spectrum in C_8F_{18} and CF_3 -c- C_6F_{11} (D) due to four equivalent protons both at 4 K and at 77 K. In contrast, the spectrum in $CFCl_3$ (A) or CF_3CCl_3 (B) has a 3×3 line structure due to two pairs of protons.¹⁷ The latter two were assigned to the radical cation having a distorted geometry where the four *exo* protons are grouped into two pairs, and the unpaired electron orbital is a modification of the $4a_2$ orbital ($4a_2'$).

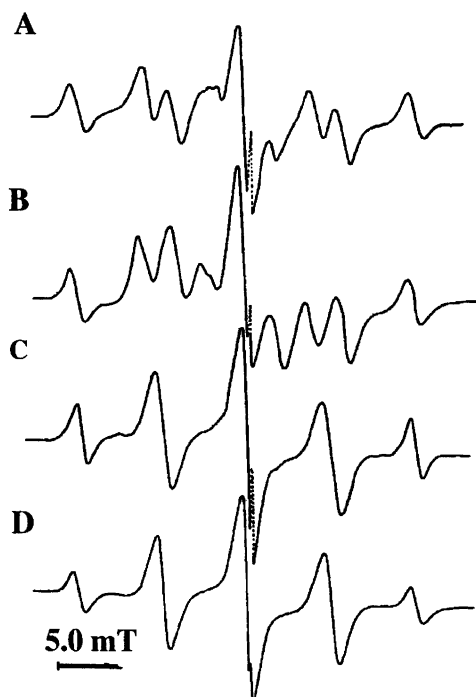
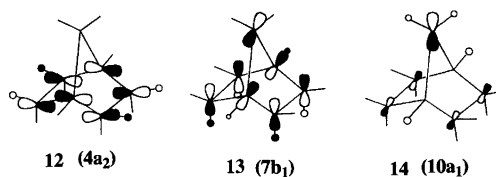
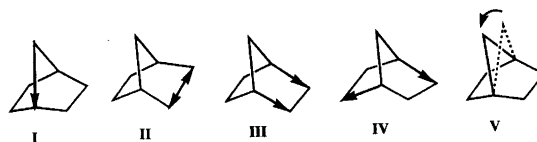


Fig. 5. EPR spectra of norbornane cation generated in: $CFCl_3$ (A), CF_3CCl_3 (B), $CFCl_2CF_2Cl$ (C), and CF_3 -c- C_6F_{11} (D), by X-ray radiolysis at 4 K. Observations were made at 4 K after annealing at 77 K. The spectra are arranged from the system with the larger distortion.



From a precise analysis of the lineshape, it was found that the cation in $CFCl_2CF_2Cl$ was also distorted although it shows an apparent five-line EPR spectrum. The extent of distortion in various systems can be ordered, taking advantage of the fact that the larger distortion results in a larger difference between the two hfc. Thus: $CF_3CCl_3 > CFCl_3 > CF_2ClCFCl_2 > CF_3$ -c- $C_6F_{11} \cong C_8F_{18}$. There are five possible forms as inset V shows, which satisfy the experimental observations. Although we cannot determine the mode of distortion only from the hf structures, the range of search can be reduced by the theoretical requirement, as will be discussed later.



As shown in Fig. 6, the cation in $CFCl_3$ just after 4 K irradiation shows a five-line spectrum (A), although it changed irreversibly to a 3×3 line once the sample had

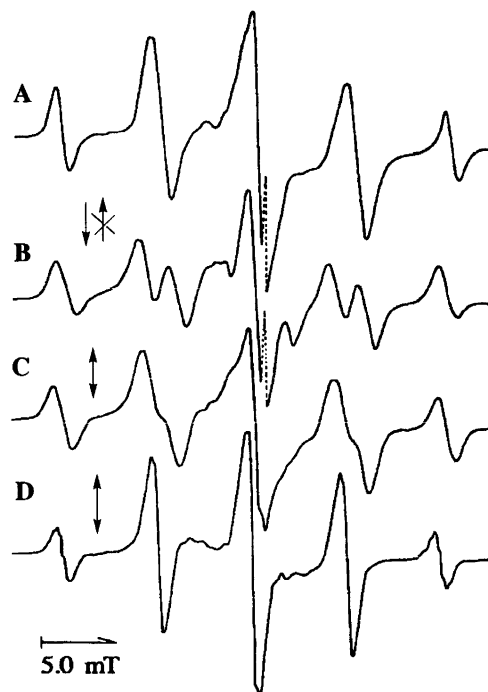


Fig. 6. Temperature dependence of the EPR spectra of norbornane cation in $CFCl_3$. Observations were made: at 4 K before (A) and after (B) annealing at 77 K, at 77 K (C), and at 130 K (D). Single and double headed arrows indicate that the corresponding step proceeds as irreversible and reversible processes, respectively.

been annealed at 50–77 K (B). At higher temperatures, the difference between the two hfc become smaller and the spectrum changes into five lines at around 130 K (D). The 3×3 lines reappeared when the sample was cooled again to 4 K. This reversible change of the spectrum is also due to an exchange process between equivalent distorted forms. This spectral change indicates that not only does the barrier height between the two mirror images increase, but also the extent of distortion upon annealing the sample at 77 K. A similar annealing effect is observed for the same cation in CF_3CCl_3 .

Causes of the asymmetric distortion: pseudo-Jahn–Teller effects and matrix interactions

The observations described above indicate that distortion of a non-JT radical cation to a conformation of a lower symmetry is quite common. The question posed to us was ‘what is the driving force of the asymmetric distortion’, since there was no theoretical requirement for these cations to distort. The characteristic features common to these radical cations are helpful in answering this question. They are (1) The direction of distortion is unique to each radical cation, but (2) the extent of distortion is dependent on the matrix; (3) annealing of the sample causes an increase in both the extent of distortion and the potential barrier between the two equivalent conformations; (4) these cations have low-lying electronic excited states. Of these, point (4) gave us most reason to attribute the cause of distortion to the ‘pseudo-Jahn–Teller effect’, which had been used to predict the direction of bond cleavage.^{18–20} According to the theory, the energy of the molecule distorted along the i th normal coordinate, Q_i is given as eqn. (1),¹⁸ where E_0 is the

$$E(Q_i) = E_0 + \frac{1}{2} V_{00}^{ii} \cdot Q_i^2 + \sum_k \frac{V_{0k}^i \cdot V_{k0}^i}{E_0 - E_k} Q_i^2$$

$$V_{00}^{ii} = \int \rho_{00} \frac{\partial^2 \phi(\mathbf{r}, \mathbf{R})}{\partial Q_i^2} d\mathbf{r}$$

$$V_{0k}^i = \int \rho_{0k} \frac{\partial \phi(\mathbf{r})}{\partial Q_i} d\mathbf{r} \quad (1)$$

energy for the undistorted configuration. The second term of eqn. (1) represents the increase in energy caused by the nuclear displacement of Q_i in the molecule without mixing of an excited electronic state, and the third term is the reduction in energy caused by redistribution of the electrons. Thus, when both the transition density ρ_{0k} and Q_i have the same symmetry and $|E_0 - E_k|$ is small, the stabilization energy is large. If further stabilization of the cation by matrix interaction is expected, the distortion along this mode is more feasible. Since the interaction changes from matrix to matrix, the distortion of a cation depends on the matrix. However, the mode of distortion is fixed if only one excited state can contribute to this process. If the matrix molecule has a high polarizability, redistribution of the charge in the radical cation may

induce further polarization in the surroundings. This feed-back loop induces rearrangement of the matrix molecules around the cation and switches the loop on again. This process constitutes the annealing effect on the distortion which is another characteristic feature of pseudo-JT distorted cations. Thus, we may call this ‘matrix-assisted pseudo-JT distortion’.

Energies of the three highest occupied orbitals ($4b_2$, $2b_1$, $6a_1$) of propane span a range of 0.3 eV, as described above.³⁴ The observed asymmetric cation is formed from the 2B_2 ground state by the b_2 distortion. Therefore, from the symmetry requirement of the above theory ($b_2 \times b_2 \times a_1 = a_1$), this distortion must be facilitated by mixing the 2A_1 excited state, which is obtained by excitation of one $6a_1$ electron to the $4b_2$ orbital, with the 2B_2 ground state. Similarly, n -pentane radical cation with C_{2v} symmetry is in the 2B_2 state and it can mix with the lowest excited state 2A_1 (the energy difference is estimated to be <0.4 eV)³⁴ by a distortion with b_2 symmetry. In the case of norbornane radical cation, five possible modes of distortion exist, which do not conflict with the observed EPR spectrum. Since the symmetry of the ground state is 2A_2 [$\dots(10a_1)^2(7b_1)^2(4a_2)^1$] and that of the lowest excited state is 2B_1 [$\dots(10a_1)^2(7b_1)^1(4a_2)^2$], the distortion should have b_2 symmetry ($a_2 \times b_1 \times b_2 = a_1$). The low excitation energy³⁵ of ca. 0.2 eV is favorable for this distortion. In fact, an INDO calculation assuming a small distortion along this direction gave hfc comparable to the observed spectrum. However, a recently reported *ab initio* calculation did not reproduce our experimental result.³⁶ A more sophisticated model where the matrix interaction is taken into consideration is thus necessary.

Paramagnetic relaxation due to the dynamics (comparison with the JT effect)

In contrast with the systems showing pseudo-JT distortion, the magnitude of distortion for JT-active cations reported so far is almost the same in different matrices. For example, ethane cation has almost the same EPR parameters in four different matrices (SF_6 , C_2F_6 , $\text{CF}_3\text{-c-C}_6\text{F}_{11}$, C_3F_8).^{1,25,37} This is also the case for both cyclohexane⁶ and benzene cations.³⁸ In addition, in the case of JT-active cations the exchange between the equivalent configurations is sometimes accelerated by annealing the system, in contrast with the pseudo-JT cations whose dynamics are decelerated by annealing. Fig. 7 shows the paramagnetic-saturation curves for both cyclohexane and norbornane cations in CFCl_3 at 4 K.³⁹ Before annealing, these two systems show almost identical saturation behavior, thus the exchange is not rapid in both systems. After annealing at 77 K, the dynamics of the cyclohexane cation are greatly accelerated as clearly indicated by the straight line in Fig. 7, but those of the norbornane cation are inhibited and thus the EPR absorption saturates at low power. This difference is explained as follows. In the case of a JT-active molecule, the matrix molecules work to inhibit the distortion and

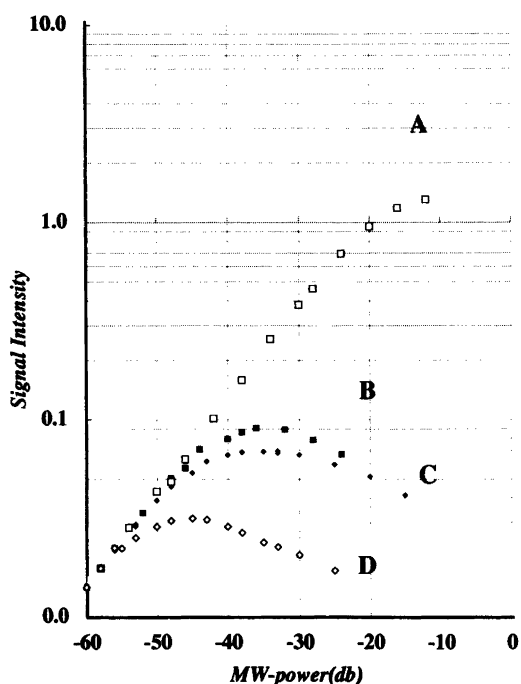


Fig. 7. Saturation behavior of the EPR absorptions of cyclohexane (A,B) and norbornane (C,D) cations generated by X-ray radiolysis at 4 K. Observations were made at 4 K before (B,C) and after (A,D) annealing at 77 K. Full power (0 db) of the spectrometer is 0.2 W, which corresponds to an H_1 field of 0.085 mT.

thus the strain energy is removed upon annealing. In the case of pseudo-JT-distortion which is partly due to the interaction with the matrix molecules, annealing makes the interaction stronger and the cation molecule is stabilized more. It is quite natural that the more distorted cation has weaker dynamics. We also observed a very short paramagnetic relaxation time for the propane cation in C_3F_8 before annealing.

The twisted structure of the ethylene cation

Recently we detected the ethylene radical cation²⁴ in the same three matrices employed for the propane radical cation. Although the EPR spectra observed at 4 K shows no apparent 1H hfc, a clear anisotropic ^{13}C hyperfine structure was observed for the ^{13}C labeled system. Careful analysis led us to conclude that $|a(H)| \leq 0.24$ mT and $|a(^{13}C)| \leq 0.4$ mT.²⁴ If the radical cation is not twisted, $a(H)$ should be around -1.0 mT according to the spin polarization theory. On the other hand if the radical cation is twisted by 90° , $a(H)$ should be larger than $+2.0$ mT due to hyperconjugation between the p orbital and the pseudo-p-orbital on the next methylene group. Therefore we conclude that the observed small hfc for the proton is the result of cancellation between the two mechanisms due to twisting of the cation by $8-23^\circ$. This rather broad range for the twist angle comes from the fact that the sign of the hyperfine coupling is not known.

It is interesting to note that the mode of distortion

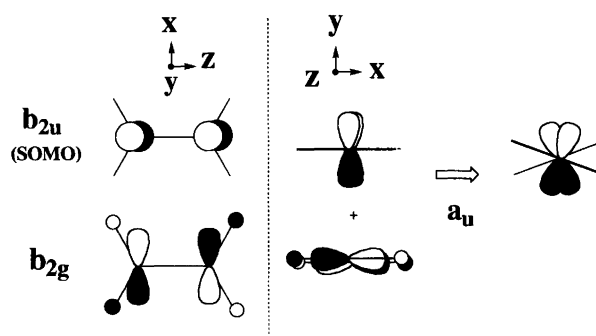


Fig. 8. Schematics of the highest two occupied orbitals of ethylene (left) and that showing the mode of mixing of these two orbitals (right) for the deformation of its cation.

can also be explained by the concept of pseudo-JT theory. Since the mode of distortion belongs to the A_u representation of the D_{2h} space group for the ethylene molecule, and the ground state of ethylene cation is in the B_{2u} state, the electronic excited state which mixes with the ground state must be B_{2g} . Since the SOMO has b_{2u} symmetry and the next highest orbital has b_{2g} symmetry as shown in Fig. 8, the excitation of one electron in the b_{2g} orbital to the SOMO yields a B_{2g} state. Although the excitation energy is as large as 2.6 eV, as determined by *ab-initio* calculation,³⁴ this mechanism operates significantly in twisting the ethylene cation. In the case of alkene cations, the strain energy generated by making the molecule planar for π -conjugation is released upon twisting; V_{0k} in eqn. (1) may thus be very large.

Before our experiment the only report of an EPR study of this cation was, to our knowledge, Shiotani's unpublished work which was cited in his review article.⁴⁰ According to this they determined the proton hfc to be 0.3 mT for the cation produced by X-ray irradiation in a neon matrix at 4 K, but failed to observe the ^{13}C hyperfine structure for the labeled system. Neither the EPR spectrum nor the details of the experiments were given.

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