

Electronic Degeneracies in Symmetric (Jahn–Teller) and Nonsymmetric Aliphatic Radical Cations: Global Topology of σ -Bonded Molecules

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Abstract: The ground-state potential surfaces of five aliphatic radical cations are investigated using a spin-pairing model. It is shown that the ground-state surface of an n -atomic system supports several stationary points (minima and transition states, including second-order ones). In addition, there are numerous nuclear configurations at which the ground state is electronically degenerate. The electronic degeneracies due to interactions between atoms bound to the same atom are either 2-fold (conical intersections) or 3-fold degenerate but not of a higher dimension. Each 3-fold degeneracy is accompanied by an even number of conical intersections (four or two). A systematic procedure for locating all of these nuclear configurations (that are in fact $3n - 8$ or $3n - 11$ dimensional hypersurfaces) is described. The model allows for the qualitative determination of the structure and charge distribution of the system at all of the stationary points and electronic degeneracies. Quantum chemical calculations confirm the predictions of the model, which is used to direct and facilitate the calculations.

I. Introduction

Alkane radical cations are of fundamental importance in the complex chemistry of interstellar clouds, and of considerable theoretical interest. Having several minima on the ground-state surface, they provide a simple example of a charge-transfer reaction, in which the charge moves across the molecular structure. A general method for analyzing the ground-state potential surface of reacting systems was presented elsewhere,¹ with an emphasis on the spin-repairing during the reaction. In this paper, the general method discussed in ref 1 is applied to this specific family of molecules.

The properties of aliphatic radical cations have been examined by several spectroscopic methods, revealing a number of ground-state isomers. The methane radical cation was the most extensively studied species. It was realized early on that the ground state of this molecule has a “fluxional” character, making it difficult to fully characterize the consequences of the Jahn–Teller distortion. Experimental ESR spectra are consistent with a ground state having six equivalent C_{2v} symmetry species rapidly interconvert via C_s -type transition states.² This characterization was fully confirmed by high-resolution optical spectra³ that allow the measurement of the tunnel splitting of the low lying vibrational levels. An upper limit of 10 ps was established for the tunneling rate. The rotational structure as deduced from PFI-ZEKE spectroscopy³ is consistent with the C_{2v} structure.

Coulomb-explosion imaging experiments⁴ are also consistent with this interpretation.

Structures of larger saturated radical cations have also been probed by ESR spectroscopy.^{5–8} A clear tendency favoring a ground-state species with a single elongated CC bond emerges from these data.

Various theoretical methods were used to study the nature of the low-lying conformers of methane and other alkane radical cations (see ref 9 for a recent compilation). The case of methane⁺ has been studied theoretically in great detail.^{10–16} All in all, the following symmetry species are found on the ground-state surface: 6 equivalent species of C_{2v} (2B_1) symmetry, 12 of C_s (${}^2A'$) symmetry, 3 D_{2d} (2A_1) species, and four each of C_{3v} (2A_1) and C_{3v} (2E) symmetry. (There is a complementary set of such structures arising from the enantiomeric structure of CH_4^+ , which is completely equivalent.¹² It is separated from the first by a relatively high barrier.) The C_{3v} (2A_1) species has a single long bond and three equivalent short ones, while the C_{3v} (2E)

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species has a single short bond and three long ones. Frey and Davidson^{15,16} analyzed the system and showed that it conforms with the Longuet–Higgins (LH) theorem:¹⁷ The phase of the electronic wave function is preserved when transported through a complete loop formed by the C_{2v} structures around the C_{3v} (2A_1) species, while the loop around the C_{3v} (2E) degenerate species inverts the sign, in agreement with the LH theorem. All of these predictions were supported by experimental work, particularly the recent high-resolution study of ref 3.

Analysis of the methane radical cation is helped by the high symmetry. Some of the larger radical cations are of lower symmetry, making a simple Jahn–Teller analysis inapplicable. A method that does not require the use of nuclear symmetry arguments is highly desirable.

Extensive *computational* analyses were performed also for the ethane radical cation.^{18–22} Work on the propane radical cation is also available.²³ In the case of the higher alkanes, computational data are available, but a comprehensive theoretical approach does not seem to exist.

The computational studies demonstrate the power of modern quantum chemical theory: many of the results were obtained before any experimental information was available. However, they were largely ad-hoc studies, requiring a separate treatment for each system. For instance, both methane and neopentane have a tetrahedral structure. The minimum energy structures of the radical cations derived from them are quite different: six equivalent C_{2v} (2B_1) minima are found in the case of methane⁺, while for neopentane⁺, the four minima have C_{3v} (2A_1) symmetry.

The goal of this paper is to offer a basis for a unified understanding of the properties of alkane radical cations. It is shown that in all systems studied, 3-fold degenerate points exist on the ground electronic state potential surface, *independent of spatial nuclear symmetry*. The origin of these degeneracies is clarified: they arise naturally from a four-state model and the permutational symmetry of the seven valence electrons bonding a carbon atom to its neighboring atoms. Motions along certain nuclear coordinates reduce the order of the degeneracy, leading to conical intersections (2-fold degenerate levels) and to nondegenerate structures on the ground-state surface. Nuclear symmetry plays no role in this model, which applies to all aliphatic radical cations.

In general, there are several minima on the ground-state potential. The barriers between these minima are small for C_1 and C_2 systems (methane and ethane) and larger for C_n ($n \geq 3$). In the latter systems, thermally activated charge-transfer reactions can take place on the ground-state potential surface. An interesting result is the fact that for the C_n ($n \geq 3$) systems, the charge-transfer reaction connecting two minima can take place along two nonequivalent routes. One of them is a phase-preserving route (with an “aromatic” transition state), and the

other is a phase-inverting route (with an “antiaromatic” transition state). The latter is found to have a lower barrier.

II. Theoretical Background

The basic assumption of the method (for more complete information, see ref 1) is that minima on the ground-state potential surface may be found by considering the spin-pairing of valence electrons. It is assumed, in the spirit of the Hückel approximation,²⁴ that the energy of the system is minimized if the chemical bond between two neighboring atoms is strengthened. The central role of the two-electron bond, recognized by Lewis,²⁵ is the basis for the use of Lewis structures to depict chemical compounds.

Ionization removes one of the valence electrons. Because in the systems considered in this paper all valence electrons are paired in single bonds, the resulting cation has one carbon atom bonded by seven electrons to its neighbors. This leads to a four-state system¹ and to a triple degeneracy. It is shown that this triply degenerate state can be used as a starting point for the description of the whole ground-state landscape of the ion, including conical intersections, minima, and transition states. Any of these structures can be reached from a 3-fold degeneracy by a monotonically declining trajectory along an appropriate coordinate.

The five radical cations discussed in this paper may be contemplated as being formed by successively substituting the H atoms of methane by methyl groups around a central carbon atom. In methane, all valence electrons are located in C–H single bonds. In higher alkanes, they may be either in C–H or in C–C bonds. Removal of a single electron from one of the bonds can lead initially to several *basic structures* in which the positive charge is localized on one of the bonds. For an alkane of the structure C_nH_{2n+2} , there are $3n + 1$ basic structures: in $n - 1$ of them the charge is on a CC bond, while in $2n + 2$ structures it is on a CH bond. Because of the lower ionization potential of a carbon atom as compared to a hydrogen atom, the CC-centered ions are expected to be energetically more stabilized than the CH-based ions. Another important factor is stabilization, due an allyl-type resonance, between two neighboring CH or CC bonds.²⁶ The spin-paired structures (shown schematically in Figure 1 for the case of propane⁺) are used as the basis functions to set up the Hamiltonian matrix of the system as a $(3n + 1) \times (3n + 1)$ matrix.

III. Anchors and Matrices

For the purpose of this paper, it is convenient to discuss molecules as an assembly of atoms that are bound by two spin-paired electrons. Different spin-pairing arrangements are termed anchors, and a chemical reaction is defined as a change of the spin-pairing scheme^{28–30}). Any system having four or more atoms can have 3-fold electronic degeneracies at a particular nuclear configuration, in which all four anchors are isoenergetic – these are, by definition, four-state systems.¹ At other nuclear geometries, only three, two, or none of the anchors are

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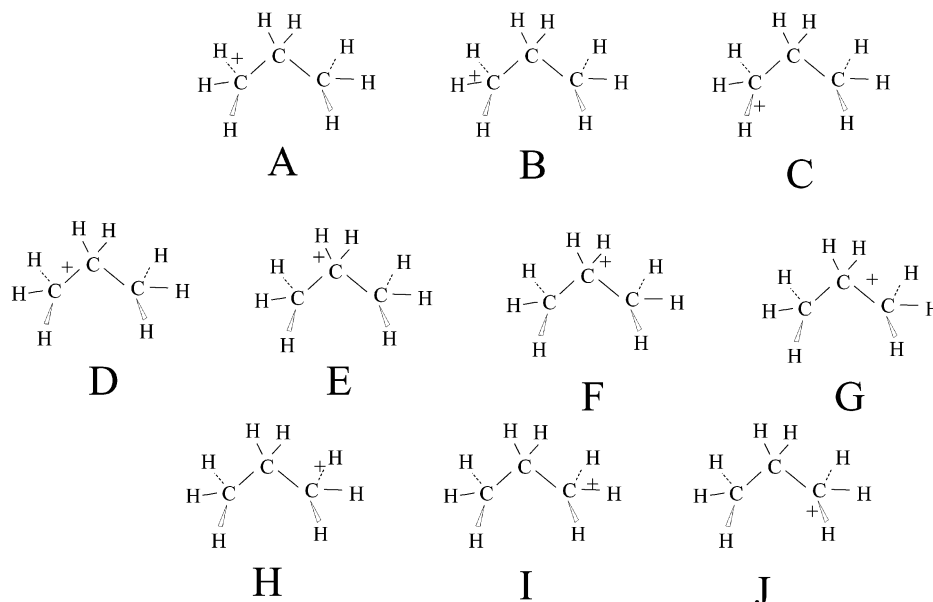


Figure 1. The 10 anchors of propane⁺. They differ by the spin pairing of the σ electrons that form the bonds.

isoenergetic. These possibilities can be checked systematically, leading to other significant points on the ground-state potential surface.

An effective way of doing this is to start at the geometry where all four anchors are isoenergetic. One type of distortion away from this point keeps three of the anchors isoenergetic, causing the secular matrix to be divided into 3×3 and 1×1 matrices. There are four possible coordinates for these “3 + 1” distortions. At the nuclear configuration Q_{PRS} in which, say, the three anchors P, R, and S are equivalent, the resulting 3×3 Hamiltonian submatrix has the form III.1.

$$\begin{Bmatrix} A - E & B & B \\ B & A - E & B \\ B & B & A - E \end{Bmatrix} \quad (\text{III.1})$$

$$\langle \phi_P | H | \phi_P \rangle = \langle \phi_R | H | \phi_R \rangle = \langle \phi_S | H | \phi_S \rangle = A \quad (\text{III.2})$$

As shown in ref 1, the off-diagonal elements are equal at this point:

$$\langle \phi_P | H | \phi_R \rangle = \langle \phi_P | H | \phi_S \rangle = \langle \phi_R | H | \phi_S \rangle = B \quad (\text{III.3})$$

The 3×3 matrix can be diagonalized, leading to a doubly degenerate state whose energy is $A - B$ and a nondegenerate state with energy $A + 2B$.¹ Thus, at this geometry, the system may have a degenerate electronic ground state and two electronic excited states for each of the possible “3 + 1” distortion coordinates.

Another type of distortion away from the 3-fold degeneracy point keeps only two of the anchors isoenergetic, causing the secular matrix to be divided into a 2×2 submatrix and two 1×1 matrices.¹ There are three possible “2 + 2” distortion

coordinates. For each of these options, diagonalization of the 2×2 matrix leads to four states whose energies are $A' - B'$, $A' + B'$, $A'' - B''$, and $A'' + B''$. The only further distortion possibility is a case of no interaction between any of the anchors, in which case the four anchors lie in separate local minima.

This scenario points to a method for finding the coordinates that lead to critical “points” (minima, transition states, degeneracies) on the ground-state potential surface.

For a tetrahedral carbon atom substituted by four different moieties, these coordinates are determined by the different possible subdivisions of the basic 4×4 matrix into submatrices: four possible three-way partitions which lead to four “3 + 1” coordinates, and three possible two-way partitions, involving, in general, three different “2 + 2” coordinates. In the case at hand, where there are only two different substituents (H atom and a methyl group), the following coordinates are to be considered.

First, we consider the “3 + 1” coordinates – changing the distances between the central atom and the others in a way that keeps three anchors isoenergetic: (1) for methane and neopentane, one coordinate type that leads to four equivalent structures; (2) for ethane and isobutane, two coordinate types, one of which leads to three equivalent structures, the other to two equivalent alternatives; and (3) for propane, two coordinate types, each leading to two equivalent alternatives.

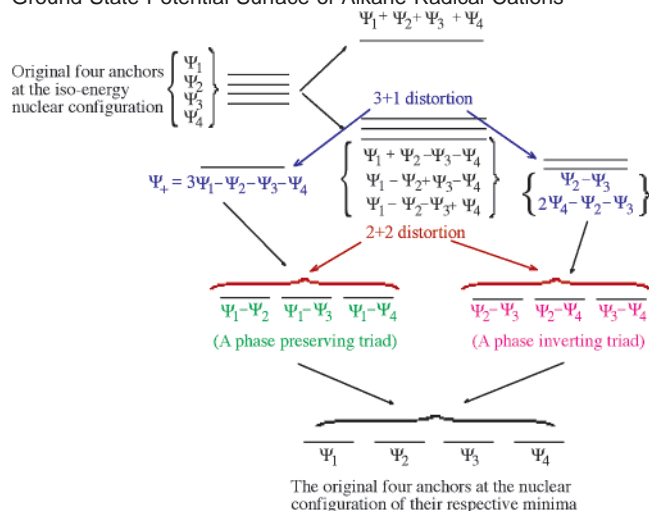
Second, we consider the three “2 + 2” coordinates – changing the distances between the central atom and the others in a way that keeps two pairs of substituents isoenergetic: (1) for methane and neopentane, one coordinate type that leads to three equivalent structures; (2) for ethane and isobutane, one coordinate type that leads to three equivalent structures; and (3) for propane, two coordinate types, one of which leads to two equivalent alternatives.

IV. Analysis of Individual Molecules

IVa. General Considerations. In this section, the methods described above are applied to analyze the ground-state potential surface of the five aliphatic radical cations. Using the 3-fold

(30) For a discussion of anchors, see refs 28 and 29. Anchors are most easily visualized as valence bond species, in which all possible structures of a given spin pairing arrangement are included. In particular, it includes both covalent and ionic structures. An anchor may have a minimum, but quite often a minimum is obtained only if a combination of several anchors is constructed (e.g., benzene). See also: Coulson, A. C. *Valence*, 2nd ed.; Oxford University Press: London, 1961; Chapter 5.

Scheme 1. A Schematic Representation of the Procedure Used To Locate Electronic Degeneracies and Critical Points on the Ground-State Potential Surface of Alkane Radical Cations^a



^a Starting with the diabatic basis set of four isoenergetic anchors, whose wave functions are Ψ_1 , Ψ_2 , Ψ_3 , and Ψ_4 , diagonalization of the Hamiltonian matrix leads to a nondegenerate excited state and a 3-fold degenerate ground state. A “3 + 1” distortion (see text), marked in blue, leads to two ground-state species (shown) and two excited states (not shown). One of the ground-state species is nondegenerate; the other, formed by the same distortion going in the opposite direction, is a conical intersection. A different distortion, the “2 + 2” one, converts the 3-fold degenerate state to a pair of nondegenerate states of the type $\Psi_{\text{out-of-phase}}$. This can be done in three ways, leading to six ground-state species. The wave function of each of these species is an out-of-phase combination of two of the original basis functions. Three of them can form a phase-preserving triad (see text); the other three form a phase-inverting triad. The latter can be obtained from the conical intersection by an appropriate distortion. The phase-preserving triad can be combined to form the nondegenerate Ψ_+ . The lowest line shows the original four basis wave functions: any two of the six $\Psi_{\text{out-of-phase}}$ wave functions having one basis wave function in common can be combined to yield that wave function back. The global minimum is either one of the basis anchors or the species represented by $\Psi_{\text{out-of-phase}}$.

degenerate state as a starting point, we obtained species generated by “3 + 1” and “2 + 2” distortions.

In all cases, four basic anchors, obtained by placing the positive charge on a bond connecting the central carbon atom to one of its four nearest neighbors, are considered. These structures have equal energies at certain nuclear geometries.¹ Let us denote the electronic wave functions of the anchors at this point by Ψ_i ($i = 1-4$). The general procedure is shown in Scheme 1.

Diagonalization of the 4×4 matrix leads to a nondegenerate excited state, constructed from the in-phase combination of the four basic Ψ_i 's, and a 3-fold degenerate ground state (see ref 1). The wave functions of these states may be written as linear combinations of those of the original anchors (neglecting normalization) as

$$\Psi_{3\text{-fold}} = \begin{cases} \Psi_1 + \Psi_2 - \Psi_3 - \Psi_4 \\ \Psi_1 - \Psi_2 + \Psi_3 - \Psi_4 \\ \Psi_1 - \Psi_2 - \Psi_3 + \Psi_4 \end{cases}$$

$$\Psi_{\text{in-phase}} = \Psi_1 + \Psi_2 + \Psi_3 + \Psi_4$$

Curled brackets denote wave functions of degenerate states. The three degenerate wave functions chosen are orthogonal.

The “3 + 1” distortions remove the 3-fold degeneracy, and each of them results in two ground-state species (Scheme 1):

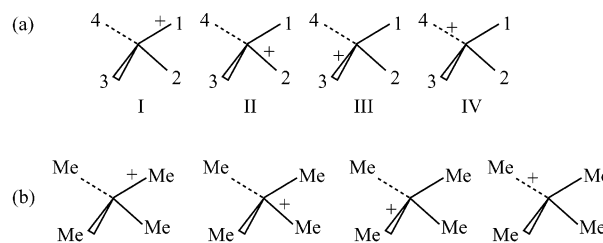


Figure 2. (a) The four anchors of methane^{•+}. (b) The four anchors of neopentane^{•+} (out of 16 possible) used in the model.

one (Ψ_+) is a nondegenerate state obtained by the in-phase combination of the three, the other, 2-fold degenerate, is obtained by out-of-phase combinations.

$$\Psi_{2\text{-fold}} = \begin{cases} (\Psi_4 - \Psi_2) + (\Psi_4 - \Psi_3) \\ \Psi_2 - \Psi_3 \end{cases} = \begin{cases} 2\Psi_4 - \Psi_2 - \Psi_3 \\ \Psi_2 - \Psi_3 \end{cases}$$

$$\Psi_+ = (\Psi_1 - \Psi_2) + (\Psi_1 - \Psi_3) + (\Psi_1 - \Psi_4) = 3\Psi_1 - \Psi_2 - \Psi_3 - \Psi_4$$

The two degenerate wave functions are chosen to be orthogonal.

The “2 + 2” distortions also remove the degeneracy of the 3-fold state, yielding each of the six possible wave functions (on the ground-state potential surface) that are out-of-phase combinations of the original anchors:

$$\Psi_{\text{out-of-phase}} = \Psi_1 - \Psi_2; \quad \Psi_1 - \Psi_3; \quad \Psi_1 - \Psi_4; \\ \Psi_2 - \Psi_3; \quad \Psi_2 - \Psi_4; \quad \Psi_3 - \Psi_4$$

The six resulting functions may be divided into two triads. One consists of three wave functions having a common factor (Ψ_1 in this case). In the second triad, the common factor does not appear at all. Inspection shows that Ψ_+ is formed by the in-phase combination of the first triad and $\Psi_{2\text{-fold}}$ is formed by the out-of-phase combination of the latter triad.

Finally, proper combinations of two $\Psi_{\text{out-of-phase}}$ wave functions recover the original anchors.³⁰

Scheme 1 will be the basis for the analysis of all individual radical cations.

The qualitative discussion is illustrated and supported by quantum chemical computations, carried out using the Gaussian program suite.³¹

IVb. Highly Symmetric Systems: $\text{CH}_4^{\bullet+}$ and $\text{C}(\text{CH}_3)_4^{\bullet+}$.

The two neutral molecules are tetrahedral around the central carbon atom. The four basic spin-paired structures of $\text{CH}_4^{\bullet+}$, in which the charge is localized on one CH bond, are shown in Figure 2a. The analogous structures of $\text{C}(\text{CH}_3)_4^{\bullet+}$ are shown in Figure 2b.

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These four structures are isoenergetic at the tetrahedral geometry of the Franck–Condon region. The resulting triply degenerate state and nondegenerate state are expected on the basis of the discussion in ref 1. Obviously, they are also obtained by standard group-theoretical treatment of the T_d group. They span a four-dimensional reducible representation Γ_{red} of the T_d group, which decomposes into two irreducible representations (irreps):

$$\Gamma_{\text{red}} = T_2 + A_1$$

The case of the methane radical cation was analyzed in detail;^{10–16} results obtained by our model agree with previous work.

The four “3 + 1” distortions (t_2 distortion) are energetically equivalent in this case, leading each to two pairs of states of C_{3v} symmetry. As Figure 3 shows, in the case of CH_4^+ distorting leftward, this results in three short CH bonds and one long one; going right, three long CH bonds and one short bond result. A long bond indicates the (partial or complete) removal of a binding electron from a bond.

In the more stable structure (i.e., on the ground state), the positive charge tends to dwell on the elongated bond(s). In the excited states, the situation is reversed – the charge tends to localize on the short bonds. In addition, the valence angle between bonds that carry the charge tends to be smaller than the tetrahedral angle ($\sim 109.5^\circ$), due to the reduced repulsion between the valence electrons. These two features will be used to analyze the computed geometries. Therefore, in the left-hand pair, the nondegenerate state is the ground state, and in the right-hand pair, the doubly degenerate species is on the ground state. Because there are four possible “3 + 1” distinct distortions, four ground-state species are expected. An analogous situation holds for $\text{C}(\text{CH}_3)_4^+$.

Figure 3b shows the effect of one of the three “2 + 2” distortions (e type in T_d), again exemplified in the case of methane⁺. Because of the high symmetry of the molecule, the left-going and the right-going distortions lead to equivalent structures. The resulting ground-state C_{2v} structures (whose wave functions are $\Psi_{\text{out-of-phase}}$ of Scheme 1) have two longer bonds (on which the charge lies) and two shorter ones, which are essentially not charged. As shown in the figure, for each ground-state minimum, there are three nondegenerate electronic states. Consider the right-hand side, in which the charge is located on the CH1 and CH2 bonds (these bonds define the xy plane). The electronic wave function of the ground state in this case transforms as the B_1 irrep of the C_{2v} group. It is represented to a good approximation by the out-of-phase combination $\psi_1 - \psi_2$. In the first excited state, the charge is located on the two shorter bonds (CH3 and CH4); it is represented by the out-of-phase combination $\psi_3 - \psi_4$ (B_2 irrep). The third state is another electronically excited one, whose wave function is constructed from in-phase combinations ($\psi_1 + \psi_2$ and $\psi_3 + \psi_4$) of the basic functions (transforming as the A_1 irrep). Distortion in the opposite direction leads to an analogous situation, except that the ground-state function is now $\psi_3 - \psi_4$ (B_2) and the first excited state transforms as B_1 . The second excited state is again constructed from in-phase combinations of the basic functions.

In all, the three possible “2 + 2” distortions lead to six equivalent structures on the ground-state surface, labeled as I-II, I-III, I-IV, II-III, II-IV, and III-IV. Together, the “3 + 1” and

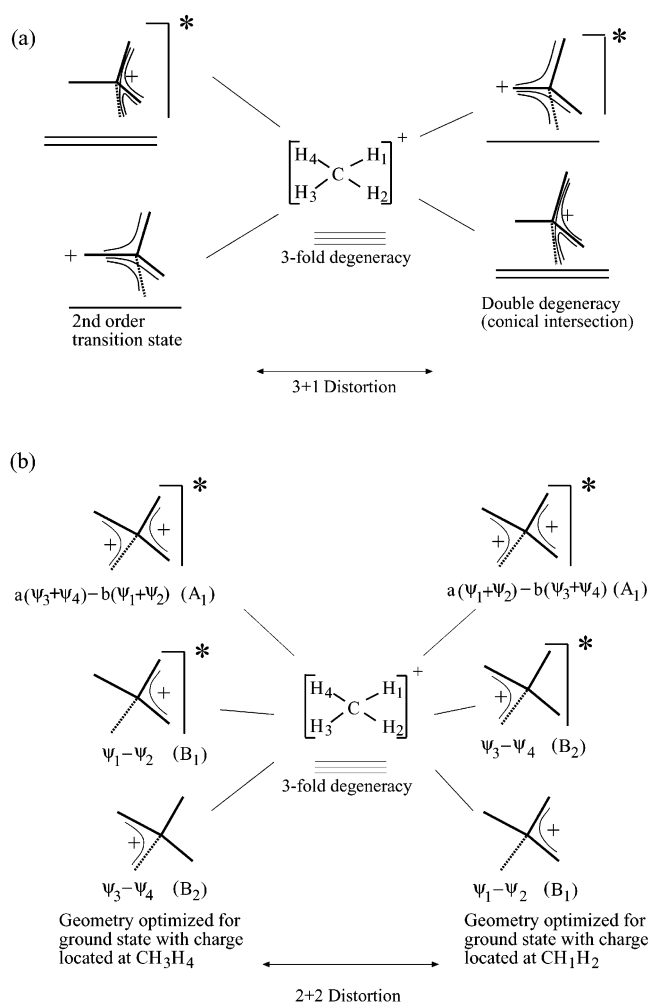


Figure 3. (a) The effect of distorting the 3-fold degenerate structure of methane⁺ along one of the “3 + 1” coordinates. On the left, the resulting nondegenerate ground-state species has one long bond and three short bonds, with the charge localized on the long bond. It corresponds to Ψ_+ of Scheme 1. On the right, the ground-state species is a conical intersection, with three long bonds and one short bond (corresponding to $\Psi_{2\text{-fold}}$ of Scheme 1). The curved lines (here and in the following figures) indicate the bonds among which the positive charge is distributed. (b) The effect of distorting the 3-fold degenerate structure of methane⁺ along one of the “2 + 2” coordinates. In this case, the left-going distortion has the same effect as the right-going one, due to symmetry. The ground state formed is an out-of-phase combination of two of the original anchors ($\Psi_{\text{out-of-phase}}$, Scheme 1). Two electronically excited states are also formed by this distortion; in C_{2v} symmetry, their wave functions transform as the B_1 , B_2 , and A_1 irreps. See text for further details.

“2 + 2” distortions lead to 10 ground-state species, 4 of which have C_{3v} symmetry, and 6 of which have C_{2v} symmetry. In the case of methane⁺, the six C_{2v} species turn out to be minima on the ground state, and the C_{3v} species are second-order transition states. This is due to the extra stabilization of the allyl-type structures shown in Figure 3b.

In the case of neopentane⁺, the situation is reversed – the C_{3v} species lie in minima, due to the preferential location of the positive charge on a CC bond. There are six C_{2v} transition species connecting them. It follows that the fact that in methane⁺ six equivalent ground-state minima are found, while in neopentane⁺ only four are found, is a reflection of the chance stabilization due to the nature of the CC and CH bonds. The basic physics of the two problems are the same.

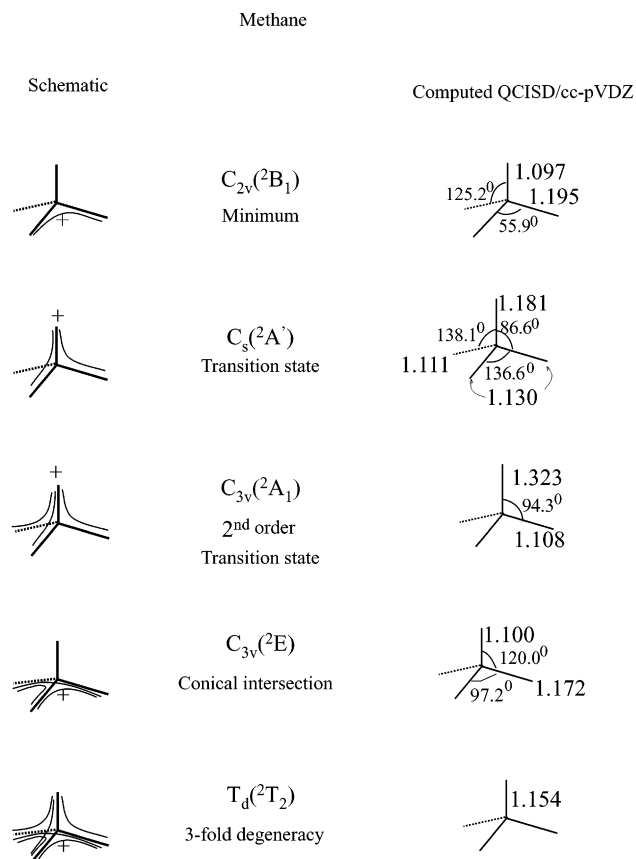


Figure 4. A comparison of the qualitative predictions of the model (left) with the computed results (right) for methane⁺. Elongated bonds and angles smaller than the tetrahedral one indicate the location of the positive charge (here and in the following figures).

The wave functions of the transition states between any two of the six ground states of methane⁺ are obtained by linear combinations of their wave functions. For instance, the wave function of the transition state between I-II and II-III may be written as $|II-III\rangle - |I-II\rangle = |2II-I-III\rangle$. The structure of this transition state is therefore of C_s symmetry: it has one long CH bond, two medium bonds, and one short bond. This was the computational result of refs 15 and 16. Here it is obtained directly from the model.

Figure 4 compares the qualitative predictions of the model with ab initio calculations for methane⁺. It is seen that the structure's 3-fold degeneracy, the conical intersection, and the transition states are all found to agree with the predictions. The same good agreement is obtained for neopentane, as seen from Figure 5.

IVc. Three-Way Systems: $C(H_3)CH_3^{+}$ (Ethane⁺) and $CH(CH_3)_3^{+}$ (Isobutane⁺). The tetrahedral cations derived from methane and neopentane may be discussed in terms of the Jahn–Teller theorem (the “3 + 1” distortion is equivalent to a t_2 distortion, and the “2 + 2” distortion is equivalent to an e distortion). In the less symmetric radical cations, such group-theoretical-based considerations do not apply. The seven basic structures of ethane⁺ are shown in Figure 6. An analysis using the whole 7×7 matrix can be carried out, but it turns out that the results are the same as those obtained by the smaller 4×4 matrix, using one of the carbon atoms as the central atom. Thus, the four-state idea works just the same as in the tetrahedrally

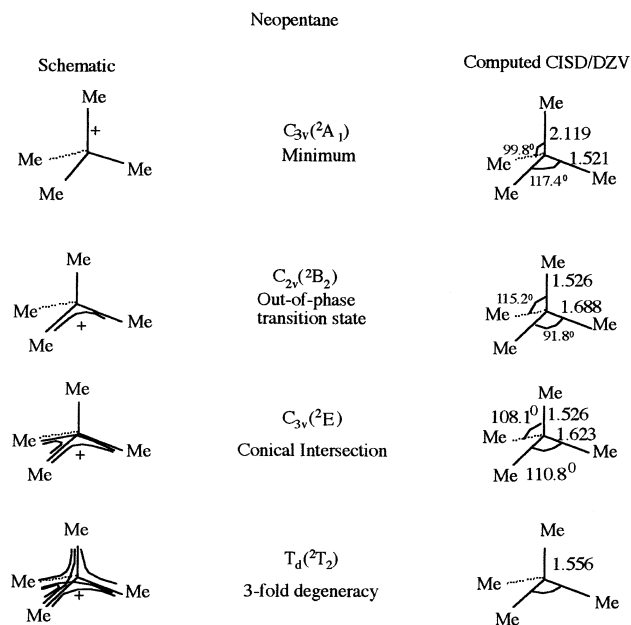


Figure 5. A comparison of the qualitative predictions of the model for isopentane⁺ using only four anchors (left) with the computed results (right).

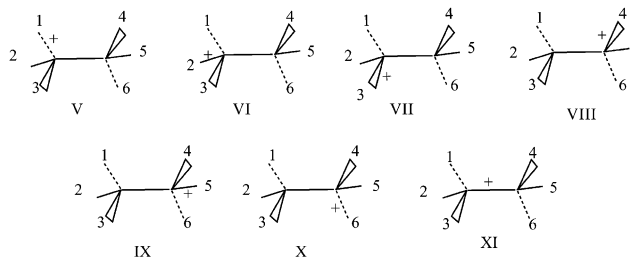


Figure 6. The seven basic anchors of ethane⁺.

symmetric radical cations. Likewise, instead of the 13×13 matrix of isobutane⁺, the simpler 4×4 matrix is used.

There are two possible “3 + 1” distortions: one leads to a lengthening of the CC bond in one direction and to its shortening in the opposite direction. The other leads to a species having a long CH bond on the ground state (Figure 7a,b, using isobutane⁺ for presentation).

Both result, in principle, in a nondegenerate state and a 2-fold degenerate state (cf. Scheme 1). The species having a longer CC bond is on the ground state; due to symmetry, this results in a $D_{3d}(^2A_{1g})$ structure. The species with the shorter CC bond is a doubly degenerate ground state. Analogous distortions hold for the ethane radical cation (not shown).

The “2 + 2” distortion leads to two species in which the positive charge is localized on a CCC group or on a CCH group. Figure 8a shows the results for ethane⁺, and Figure 8b shows the analogous case of isobutane⁺.

The energy considerations outlined above for methane⁺ hold also for the analysis of ethane⁺. The presence of a CC bond strongly affects the energy balance, because the positive charge tends to concentrate there. Motion along one of the two “3 + 1” distorting coordinates leads to a charge-centered CC bond of $D_{3d}(^2A_g)$ symmetry, which is a global minimum. The other leads to a charge-centered CH bond, analogous to that of methane⁺. This turns out to be a high-energy species that does not form a minimum. An out-of-phase combination of two such species forms a $C_s(^2A'')$ structure (as shown in Figure 9) that lies in a local minimum. A third energy minimum is due to an

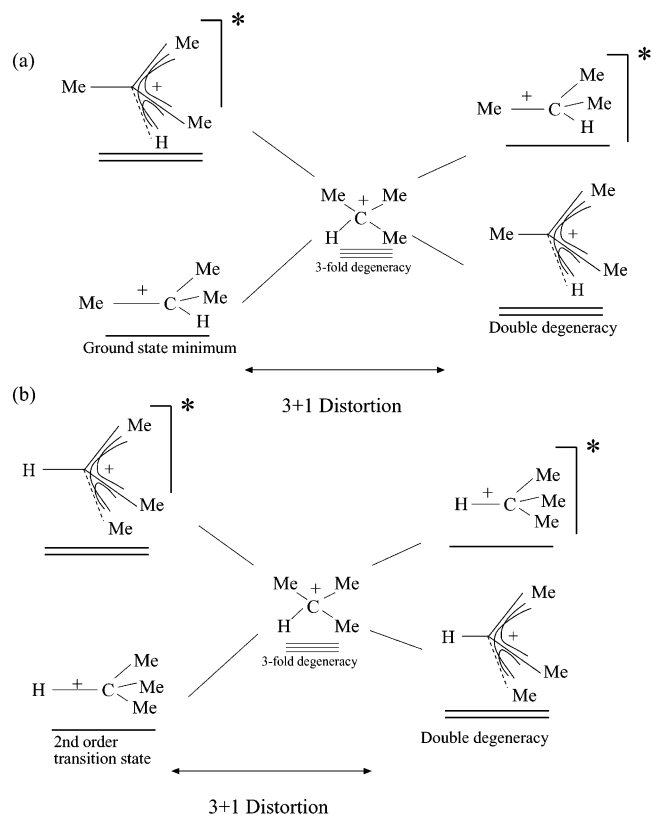


Figure 7. The effect of distorting the 3-fold degenerate structure of isobutane⁺ along two different "3 + 1" coordinates. (a) Stretching of a single CC bond (going left) leads to a stable minimum on the ground state. In the other direction, a conical intersection is obtained. (b) Putting a charge on a CH bond should lead, in principle, to a ground-state species. In practice, some charge is spread over the three CC bonds, and a second-order transition state is obtained (see text).

in-phase combination of two resonance-stabilized structures formed by the "2 + 2" distortion shown in Figure 8. Figure 10 shows how two such structures combine to form a C_{2h} ("diborane-type"²²) ground-state species. The charge is mostly on the CC bond, but it stretches somewhat to two CH bonds on the two carbon atoms. Note that the angles between the charge-carrying bonds are expected to be smaller than the tetrahedral angle.

Figure 11 compares the qualitative predictions of the model with ab initio calculations for ethane⁺. The energy difference between the "diborane" and the D_{3d} (2A_g) symmetry species is very small. Physically, both may represent a single, very shallow potential surface in which one CC bond is stretched.

The two types of conical intersections expected from the model are indeed confirmed by the calculations. In one (C_{3v} (2E) type), three CH bonds are stretched, a Jahn–Teller case. In the other (C_s (${}^2A'/{}^2A''$) type), two CH bonds and one CC bond share the charge.

In the case of isobutane⁺, there are three CC bonds that can accept the charge. This leads to three C_s (${}^2A'$) minima, in which charge is localized on a CC bond, that dominate the ground state of this ion. Minima in which charge is also located on CH bonds (partially or totally) are expected to be higher in energy. There are two types of transition states between the C_s (${}^2A'$) minima. The first is a C_s (${}^2A''$) state, formed by the out-of-phase combinations of two C_s (${}^2A'$) species. This is analogous

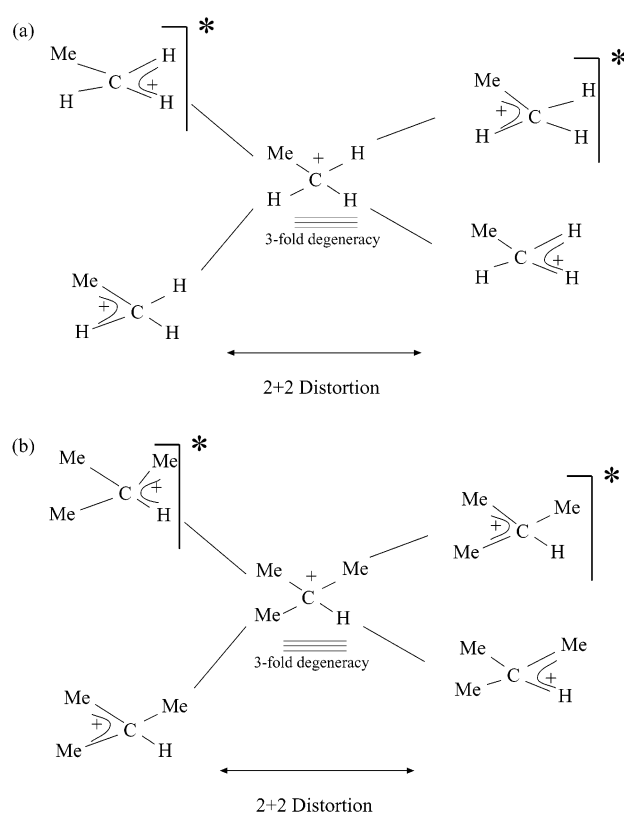


Figure 8. The results of the "2 + 2" distortions in the cases of ethane⁺ (a) and isobutane⁺ (b). In both cases, the species in which the charge is located near CC bonds are more stable than those in which the charge is situated on CH bonds. Only the lower of the two excited states formed by this distortion is shown; the other is analogous to the A_1 state shown for methane (Figure 3b).

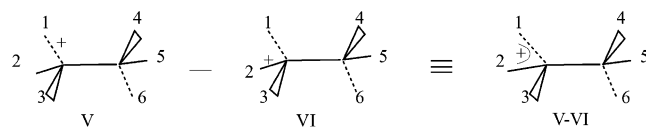


Figure 9. The expected structure of ethane⁺ in a high-energy local minimum.

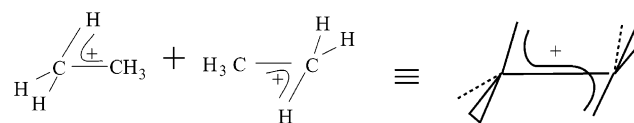


Figure 10. A scheme showing how a combination of two species whose wave functions are $\Psi_{\text{out-of-phase}}$ (see Scheme 1) leads to the formation of a "diborane" structure of ethane⁺.

to the case of methane⁺. The second is a phase-preserving transition state (C_s (${}^2A'$) symmetry) in which the two electrons of the CH bond participate (see the discussion of propane⁺).

Two types of conical intersections are found, as predicted by the two "3 + 1" distortions. One has C_{3v} (2E) symmetry and is enclosed in a loop formed by the three phase-inverting reactions converting one minimum to the other via the C_s (${}^2A''$) transition states. A secondary conical intersection (C_s (${}^2A'/{}^2A''$)) is enclosed in a loop consisting of two of these anchors. The loop is formed by two different reactions connecting two C_s (${}^2A'$) minima: one reaction is via the phase-inverting C_s (${}^2A''$) transition state, and the other is via the C_s (${}^2A'$) phase-preserving state (cf. the discussion of propane⁺ for further details).

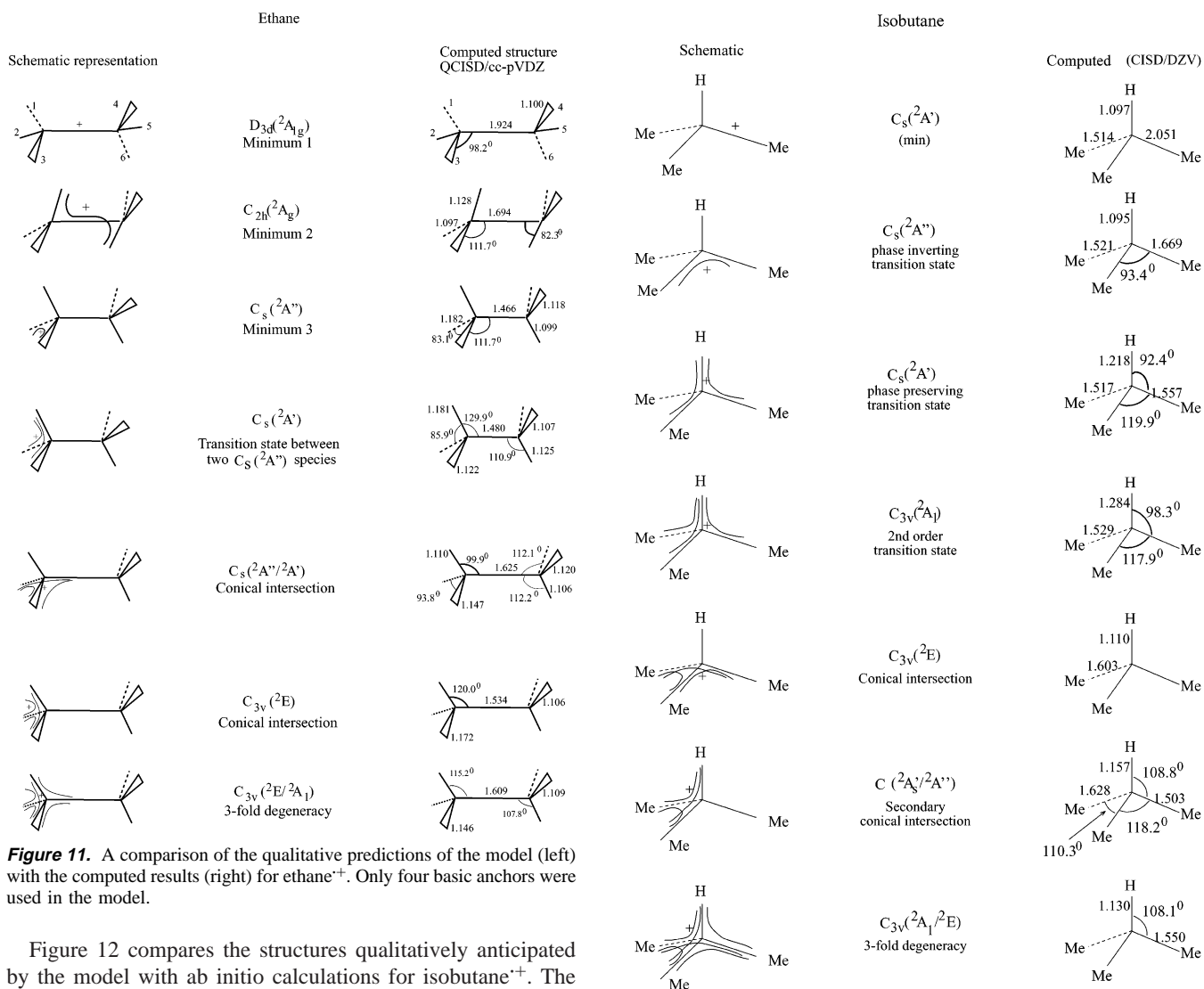


Figure 11. A comparison of the qualitative predictions of the model (left) with the computed results (right) for ethane⁺. Only four basic anchors were used in the model.

Figure 12 compares the structures qualitatively anticipated by the model with ab initio calculations for isobutane⁺. The numerical results nicely confirm the model's predictions.

IVd. Two-Fold System: The Propane Radical Cation. As in the case of other molecules having a CC bond, the stabilization of the CC-bond charge-centered species is dominant. Therefore, to a first approximation, the smaller 4×4 matrix can be used to deduce the properties of the system.

Note that the highest geometric symmetry of the propane radical cation can be C_{2v} , a group that has no degenerate irrep. Therefore, the predicted triply degenerate species resulting from the diagonalization of the 4×4 matrix must consist of three electronic states transforming according to *different* irreps. This result is indeed confirmed by computations.

Two “3 + 1” distortions are possible: in the first, the unique bond is a CC bond, and in the second, it is a CH bond (Figure 13). The first leads to two stable ground-state minima, in one direction, and to a conical intersection in the other. The second “3 + 1” distortion leads to a high-energy species with a long CH bond (two different possibilities) in one direction and to a conical intersection in the other. All of these structures lie at a higher energy than the C_s structure formed by the former “3 + 1” distortion.

Only two major minima are expected in this case – the two electromers in which charge is localized on one of the CC bonds $C_s({}^2A')$ symmetry. The “3 + 1” distortion that leads to a CH

Figure 12. A comparison of the qualitative predictions of the model, using four basic anchors (left), with the computed results (right) for isobutane⁺.

charge-centered species is expected to lie at much higher energies and may not represent a minimum. As shown in Figure 14, two “2 + 2” distortions of the 3-fold degenerate state are possible in this case. One leads to a CCC charge-centered species that is recognized as the out-of-phase combination of the two $C_s({}^2A')$ minima (Figure 15). It serves as a transition state for the out-of-phase reaction converting one species to the other.

The second “2 + 2” distorting coordinate leads to CCH charge-centered species. This species does not sustain a minimum at any nuclear configuration. Its presence is implied by a structure in which the charge is distributed among the three carbon atoms and one hydrogen atom, due to its interaction with the two CC charge-carrying anchors (see Figure 16); there are two possible ways to do so, one for each methylenic hydrogen atom. *The resulting species is another transition state between two $C_s({}^2A')$ minima.* It is an in-phase combination of the two, in which the electrons forming the CH bond participate. Its energy is expected to be higher than that of the out-of-phase transition state, as the allyl-type resonance stabilization is expected to be larger for CC bonds than for CH bonds.

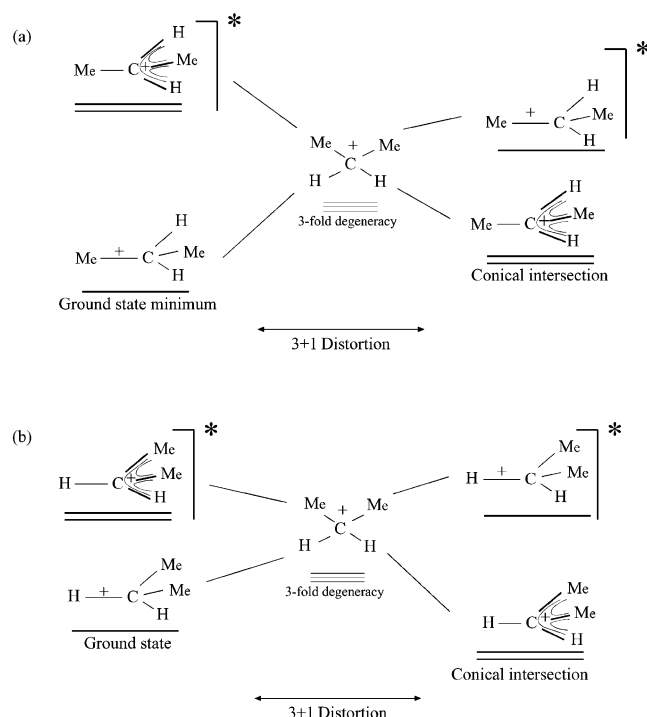


Figure 13. The effect of distorting the 3-fold degenerate structure of propane⁺ along one of the "3 + 1" coordinates. (a) A CC bond is stretched/compressed, and the charge is localized on a single long CC bond (two different possibilities); these species are the global minima having C_s symmetry. (b) A CH bond is stretched/compressed. The nondegenerate species on the ground state is not a stable minimum at any nuclear geometry. See text for details.

There is no nuclear configuration of the CCH charge-carrying anchor itself that is at an energy minimum. The only manifestation of this anchor is the stationary point in which it participates.

Using the two anchors D and F, and the three transition states, we formed three loops. One of the two phase-inverting loops is shown in Figure 17 (the other uses species 2F–D–G as the phase-preserving transition state). They encircle two equivalent degeneracies by the Longuet–Higgins theorem. A loop formed by combining the two species using the two phase-preserving transition states (Figure 18) encircles a *nondegenerate* C_{2v} species, which is a second-order transition state.

The implications of this unique situation, in which two ground-state species are connected by several transition states, are discussed in section V.

Figure 19 compares the qualitative predictions of the model with ab initio calculations for propane⁺, again indicating very good agreement.

The numerical values obtained for the energies of the calculated species for all five radical cations are collected in Table I. In all cases, a complete vibrational analysis was carried out. All normal modes of the minima were found to have real frequencies. The first-order and second-order transition states were found to have one or two imaginary frequencies, respectively. Recognizing that the electronic degeneracies are in fact multidimensional surfaces, we made no particular effort to obtain their minimum energy. In several exploratory runs that were made, it was found that the $3n - 8$ dimensional surface was fairly shallow in the vicinity of the values listed in the table. In cases where several different states are involved, the numerical

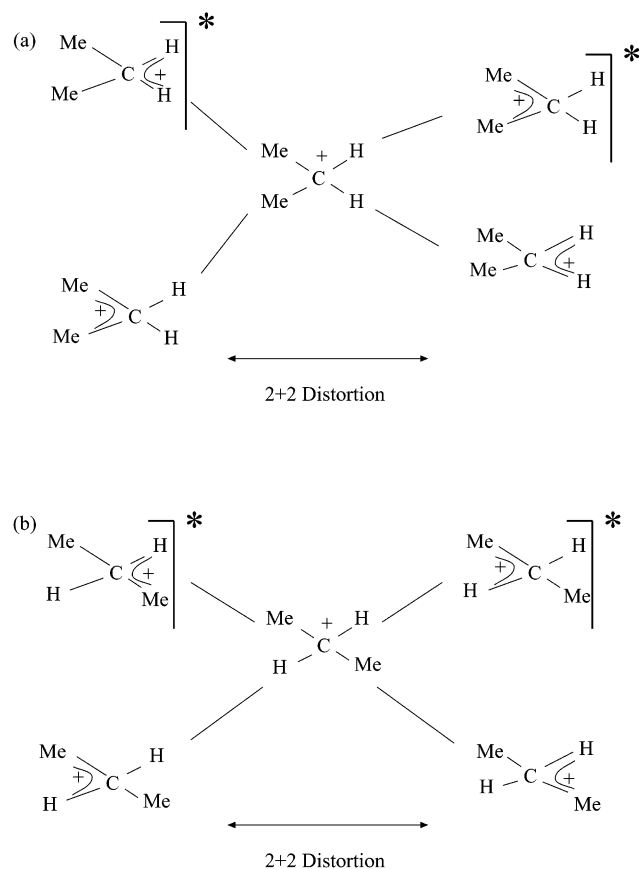


Figure 14. The effect of distorting the 3-fold degenerate structure of propane⁺ along one of the "2 + 2" coordinates. Only the lower of the two excited states formed by this distortion is shown; the other is analogous to the A_1 state shown for methane (Figure 3b). (a) Two CC bonds are stretched/compressed. The resulting species are transition states having C_{2v} symmetry. (b) A CC and a CH bond are stretched/compressed together. See text for further discussion.

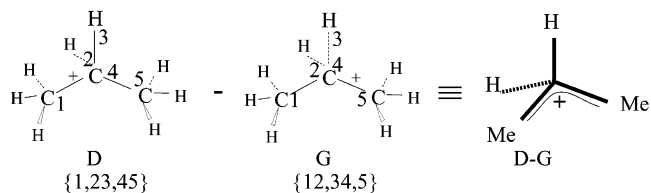


Figure 15. The structure of the C_{2v} symmetry transition state of propane⁺ formed by the out-of-phase combination of D and G (cf. Figure 1).

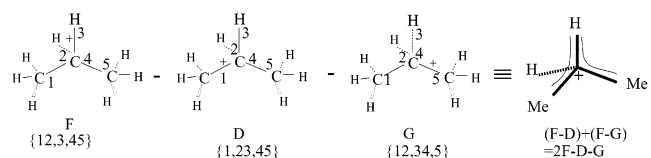


Figure 16. The combination of three anchors (D, F, and G) of propane⁺, forming a second transition state (of C_s ($^2A'$) symmetry) between the two main minima. This is a phase-preserving transition state.

search for a degeneracy was stopped when the energy difference between two states was less than 1 kcal/mol.

V. Discussion

The qualitative predictions of Scheme 1, which provides a unifying conception for the analysis of the potential surface of all radical cations, were verified by the computed results. All predicted electronic degeneracies were found. In particular, each

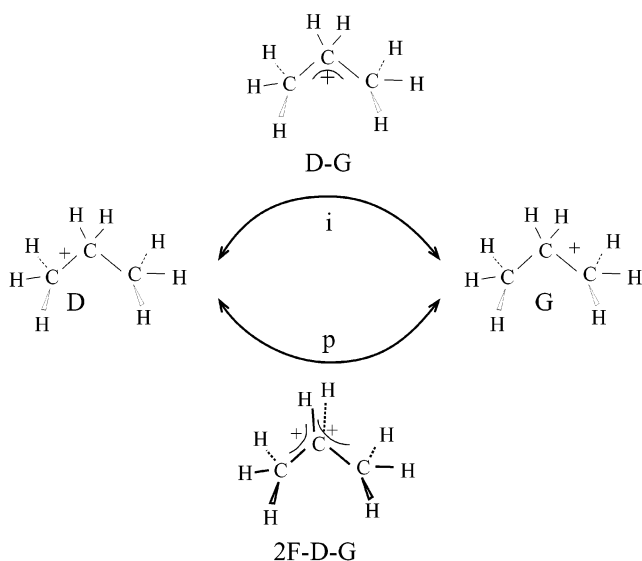


Figure 17. A phase-inverting loop formed between two minima of propane⁺, using the two different transition states.

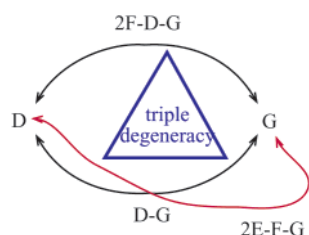


Figure 18. Two phase-inverting loops and a phase-preserving loop formed between the two major minima of propane⁺, using three transition states. The 3-fold degeneracy is encircled by these three loops.

3-fold degeneracy is surrounded by an even number of conical intersections, as expected. The computational results agree with previous work when available.^{11–20} An important new result is the fact that a 3-fold degeneracy is found in all five cations. The fact that the model-inspired computer search yielded 3-fold degeneracies in all systems suggests that the assumptions underlying the model are reasonable.

Another new feature is the fact that the reaction between two electromers can proceed along two different reaction coordinates in the case of propane and isobutane radical cations. These transition states and the conical intersections affiliated to them could not have been easily found without the guidance of the model.

The main message of this paper is that the results can be rationalized within a simple physical framework. The ground-state potential surfaces of all five alkane radical cations have many features in common (Table 1). The analysis of a seven-electron system around a single carbon atom, applied to all radical cations, was found to lead to both degeneracies and stationary points on the ground potential surface. Each four-state system has a 3-fold degenerate state, regardless of nuclear symmetry. All also have several 2-fold degeneracies (conical intersections), obtained by a “3 + 1” distortion of the four equivalent structures. The ground-state minima, and all stationary points, are reached from the 3-fold degenerate species without a barrier.

The relative stabilization of charge-carrying bonds is a key factor in determining the structures of the ground-state minima.

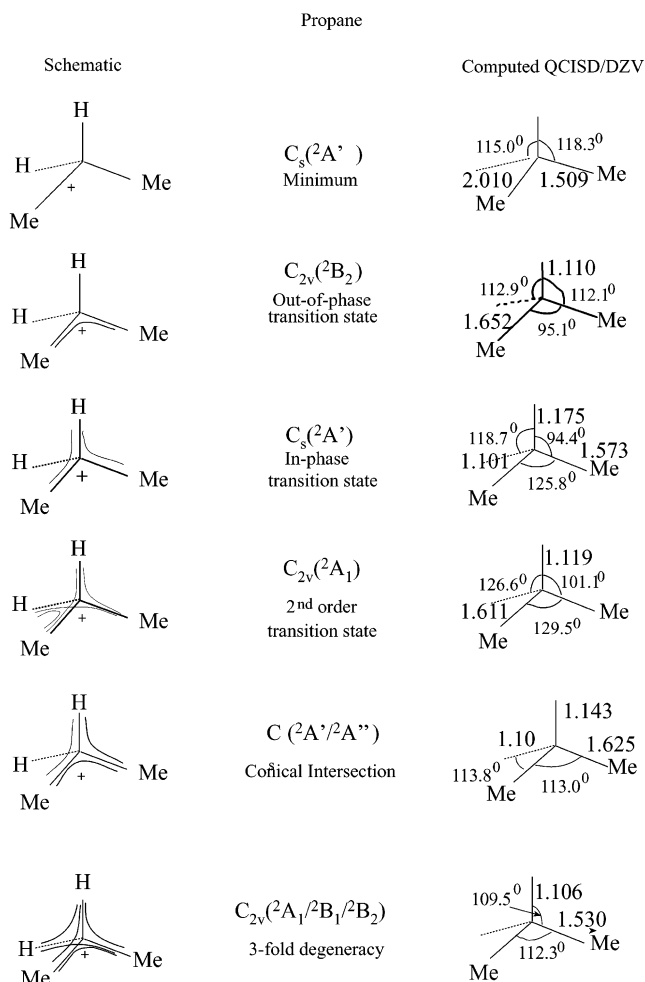


Figure 19. A comparison of the qualitative predictions of the model for propane⁺, using four basic anchors (left), with the computed results (right).

For radical cations containing three or more carbon atoms, the species carrying the charge on a CC bond are lowest in energy. Thus, it is found that the propane, isobutane, and neopentane radical cations have two, three, and four major minima, respectively. For the C_1 and C_2 species, allyl-type resonance between two bonds carrying the charge becomes important. This leads to six minima for both methane⁺ and ethane⁺.

Conical intersections lie within phase-inverting loops^{17,28,29} that can be formed by reaction coordinates connecting the different electromers. At least two minima are required to create such loops. In the case of isobutane⁺ and neopentane⁺, there are three and four minima, respectively, due to species in which the charge is localized on a CC bond. Three-anchor loops are easily formed in this case. Propane⁺ has only two such minima. Phase-inverting loops can be formed in this case only if charged species in which the charge is partially localized on CH bonds participate. As no minima involving a species in which a CH bond carries the positive charge were identified for this cation, a phase-inverting loop must be constructed using two anchors only. It was shown that this is possible because two different reaction channels, involving two distinct transition states, connect the two minima in this case (Figure 17). The role of the charge-carrying CH species is reflected in the phase-preserving transition state.

In all radical cations, the geometry of the triply degenerate state turns out to be similar to that of the neutral molecule. A

Table 1. The Calculated Relative Energies of the Main Species of the Five Radical Cations (Energies in kcal/mol, with Respect to the Minimum of Each Radical Cation)^a

species	methane ⁺	ethane ⁺	propane ⁺	isobutane ⁺	neopentane ⁺
stable minima	C_{2v} (2B_1) 0.0	D_{3d} (${}^2A_{1g}$) 0.0 C_{2h} (2A_g) 0.2 C_s (${}^2A''$) 5.6	C_s (${}^2A'$) 0.0	C_s (${}^2A'$) 0.0	C_{3v} (2A_1) 0.0
out-of-phase transition states ^b	C_s (${}^2A''$) 3.0	C_s (${}^2A''$) 9.3 C_1 (2A_1) 6.1	C_{2v} (2B_2) 4.7	C_s (${}^2A''$) 8.2	C_{2v} (2B_1) 9.7
in-phase transition states ^b	C_s (${}^2A''$) 3.0		C_s (${}^2A'$) 13.8	C_s (${}^2A'$) 16.1	
2nd order transition states ^c	C_{3v} (2A_1) 11.6	C_{2v} (2A_1) 13.8		C_{3v} (2A_1) 16.3	
conical intersections ^d	C_{3v} (2E) 27.0	C_{3v} (2E) 13.8 C_s (${}^2A''/{}^2A'$) 25.9	C_s (${}^2A''/{}^2A'$) 24.0	C_{3v} (2E) 16.3 C_s (${}^2A'/{}^2A''$) 27.2	C_{3v} (2E) 32.6
3-fold degenerate state	T_d (2T_2) 36.2	D_{3d} (${}^2A_{1g}/{}^2E$) 30.9	C_{2v} (${}^2A_1/{}^2B_1/{}^2B_2$) 32.7	C_{3v} (${}^2A_1/{}^2E$) 33.5	T_d (2T_2) 34.2

^a The level of theory was QCISD/cc-pVDZ for methane⁺ and ethane⁺, QCISD/DZV for propane⁺, and CISD/DZV for isobutane⁺ and neopentane⁺. ^b One normal mode has an imaginary frequency. ^c Two normal modes have imaginary frequencies. ^d In the case of methane⁺, propane⁺, and neopentane⁺, the two conical intersections are identical.

possible rationale is that at this geometry, the interactions between any two neighboring bonds are the same. This degenerate state is reached directly by photoionization, as a consequence of the Franck–Condon effect. It is thus the initial state in a photoionization experiment. The system will tend to distort to one of the minima and, if raised to high enough energy, to follow several dissociation routes.

VI. Summary

The main results of the analysis presented in this paper are (1) the ground state of all five aliphatic radical cations contains a 3-fold electronic degeneracy; (2) the geometry of these degeneracies is close to that of the neutral alkane; (3) an even number of 2-fold degeneracies is found for all radical cations; (4) the model predicts the qualitative structures of all radical cations at their minimum energy configurations, transition states, and electronic degeneracies, and these predictions are confirmed by high level quantum chemical calculations; (5) it follows that the central 4×4 matrix makes the major contribution to the topology of the ground state of all radical cations; and (6) the highest possible electronic degeneracy due to interactions

between moieties bound to the central carbon atom is 3-fold. In the case of large molecules, higher degrees of degeneracies are possible due to the coexistence of several noninteracting identical groups.¹

The energies of 3-fold degeneracies for all radical cations were found to be of similar magnitude, 31–36 kcal/mol. This may be a coincidence, but it may also indicate that the energy required to distort all cations to a triply degenerate state is such that the charge density in all bonds is about the same.

For the propane and isobutane radical cations, a unique finding is the fact that the charge shift reaction between two CC charge-centered minima may follow two independent routes, having two different transition states. The out-of-phase state is of lower energy.

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