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Configuration interaction calculations on the propane radical cation, $C_3H_8{}^+$

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Summary. Proton isotropic hyperfine coupling constants have been calculated for three low-energy nuclear conformations on the ground state potential surface of the propane cation, using a multireference singles and doubles configuration interaction (MR-SDCI) wave function. The lowest point found on the potential surface had C_{2v} symmetry and the electronic wave function at this point had ${}^2B_2$ symmetry. At this point, the largest isotropic coupling constant is calculated to be 88.6 G, which is in fair agreement with the experimental value of 98 G obtained in an SF_6 matrix at 4 K. No support is found for a "long-bond" ground state of lower symmetry than C_{2v}. Another C_{2v} minimum on the ground state potential energy surface was found at which the wave function had ${}^2B_1$ symmetry. At this point, two large coupling constants of 198 G and 35 G were calculated. A C_{2v} stationary point was also found on the ground state potential surface at which the wave function had ${}^2A_1$ symmetry. At this point, couplings of 86 G and 25 G were obtained. None of these agree closely with the other experimental result of couplings at both 100–110 G and 50–52.5 G which was obtained in freon matrices. It is suggested that the latter spectra might correspond to a dynamical average of two distorted ${}^2A'$ states in C_s symmetry.

Key words: Propane cation — Configuration interaction — Hyperfine coupling constants

Introduction

Radical cations of hydrocarbons are generally reactive and short-lived, and have traditionally been difficult to observe experimentally. However, during the last decade, the technique of matrix isolation electron spin resonance (ESR) spectroscopy at low temperatures has opened up new possibilities for their study. Considerable information about structure, dynamical behavior and reactions of hydrocarbon radical cations has been obtained in this way during a relatively short time period [1].

It is desirable that the matrices used in these experiments be chemically inert, so the most commonly used matrices include the rare gases, SF_6, and mixed flurochlorohydrocarbons (freons). In most cases studied so far, the results of the experiments are essentially independent of the choice of the matrix, except for minor variations in the hyperfine coupling constants (hccs) derived from the ESR spectra. Cases with manifestedly strong interactions between the solute molecules (cations) and the matrix have been reported [2], but only for compounds containing at least one heteroatom, such as oxygen.

The results obtained by Iwasaki and coworkers [3] for the propane cation are therefore unique, in that two qualitatively different ESR spectra were obtained when different matrices were used. In SF_6, a spectrum arising from two equivalent protons with isotropic hccs of 98 G was obtained, whereas the spectra recorded in a number of freon matrices indicate the presence of two equivalent protons with a hcc of 100–110 G and four equivalent protons with 50–52.5 G [3, 4]. On the basis of semiempirical INDO calculations, combined with measurements on partially deuterated samples, Iwasaki and coworkers associated the first spectrum with the $^2B_2$ ground state of the propane cation and the second type of spectrum with the $^2B_1$ state [5].

Later *ab initio* UHF calculations [4] have supported the first of these assignments, while throwing some doubt on the second one. The accuracy of these calculations was, however, insufficient to either confirm or disprove, with certainty, the suggested assignments. We have therefore repeated the calculations using more accurate methods developed recently [6], in order to attempt a more conclusive interpretation of the observed spectra.

Method

Wave functions and hyperfine coupling constants were calculated with the MELD program suite [7] using a basis set of contracted Gaussians. For all CI calculations, the (13*s*, 8*p*) primitive basis given by van Duijneveldt [8] was used for carbon and his (10*s*) basis was used for hydrogen. The carbon basis was contracted to [5*s*, 4*p*] and augmented by a *d*-type polarization function with exponent 0.75, whereas the hydrogen basis was contracted to [4*s*] and augmented by a *p*-type polarization function with exponent 1.0. The quality of this basis is comparable with the largest basis sets investigated in [6] and should be sufficient to ensure acceptably small errors in the electron density values at the nuclei. Before performing the SCF calculations, the spherically symmetric combinations of the six Cartesian *d*-components were removed from the basis, giving a total of 122 contracted basis functions.

The CI calculations included all single excitations and the most important double excitations (SDCI), as selected by second order perturbation theory [9] using a RHF or multireference zeroth order wave function. The 1*s* orbitals of the carbon atoms were treated as core orbitals (i.e., were kept doubly occupied during the excitations), which is a physically reasonable constraint since our primary interest was in the proton hccs. Before performing the CI, the virtual orbitals were transformed to K-orbitals [10], which previously have been shown to mimic the frozen natural orbitals of the system resulting in faster convergence in the CI.

Since no experimental geometries are available for the propane cation, C_{2v} constrained optimum geometries for three different wave function symmetries ($^2B_2$, $^2A_1$, $^2B_1$) were optimized using the GAUSSIAN-82 [11] program. This was done with and without polarization functions and also with and without the inclusion of the MP2 electron correlation energy. Figure 1 shows a plot of the singly occupied orbital for each of the states under consieration (see also Fig. 4 of [4]). The atom numbering scheme and molecular orientation are shown in Figure 2. At each of the three resulting geometries, the resulting wave function was the ground state wave function. Hence, all energies are actually points on the global ground state potential energy surface.

To determine an appropriate level of accuracy for the CI calculations, test calculations were performed for one of the symmetries ($^2A_1$) at a fixed geometry, with different numbers of configurations included. The results are shown in Table 1. The total number of configurations used in each calculation is given in column 3 and the corresponding energy criterion in the perturbation theory selection in column 2. As can be seen from the table, an increase of the number of configurations from 30,000 to 65,000 causes only minor modifications in the hyperfine coupling constants. It was therefore judged that the smaller number would be adequate for the remaining calculations for the other states, as well as for $^2A_1$. Shorter CI expansions were not tried, even though it is possible that equivalent results could have been obtained with fewer configurations.

The result of a SDCI calculation with a multiconfiguration reference function (MR-SDCI) is also shown in Table 1. It is apparent that the use of a 3-configuration reference function gives only minor modifications of the a_i values. This

Table 1. Dependence of the isotropic proton hyperfine coupling constants for the $^2A_1$ state of the propane cation on the size of the CI expansion[d]

Type of CI	P.T. threshold[a]	Number of configurations	$a_1{}^c$	$a_2{}^c$	$a_3{}^c$
SDCI	$8.0E-06$	30,201	83.1	8.7	23.6
	$5.0E-06$	48,991	83.1	8.7	23.5
	$3.0E-06$	65,396	82.8	8.7	23.5
MR-SDCI[b]	$9.0E-06$	29,906	83.5	8.8	23.7

[a] The second order perturbation theory energy threshold (a.u.) used for selecting configurations to be included in the variational calculation. (1 a.u. = 27.21 eV)

[b] Three configurations were used in the reference space

[c] Hyperfine coupling constants at proton type 1, 2, and 3 (in Gauss)

[d] Calculated at the UHF/6-31G optimized geometry

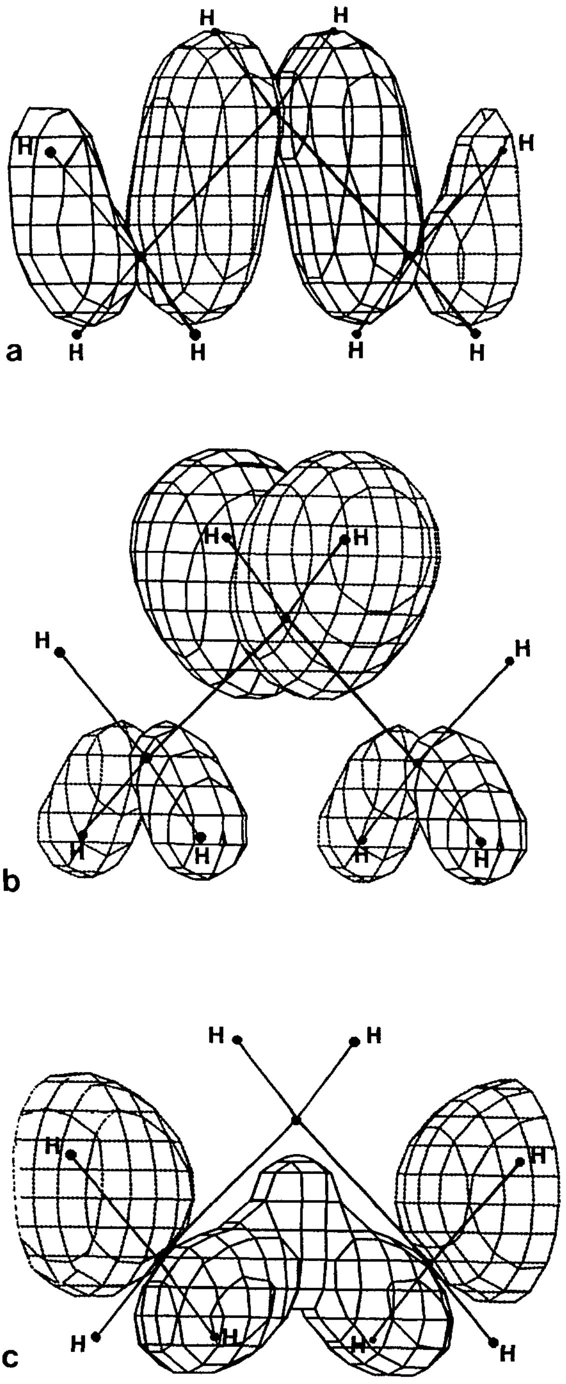

Fig. 1. 70% probability surfaces for the singly occupied orbitals in the $^2B_2$ (**a**) $^2B_1$ (**b**) and $^2A_1$ (**c**) states of $C_3H_8^+$

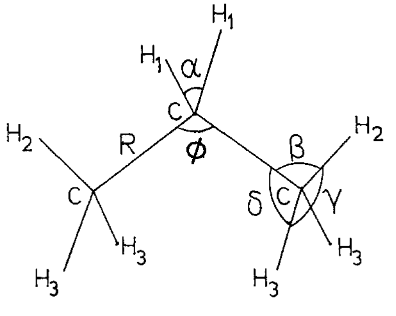

Fig. 2. Definition of the geometrical parameters α, β, γ, δ, ϕ and the atom labelling convention

was not unexpected since the SDCI expansion was strongly dominated by the RHF configuration with coefficient 0.9405. This is true not only for the $^2A_1$ symmetry, but also for the $^2B_1$ and $^2B_2$ symmetries. Therefore, in the remaining work, only SDCI expansions with a single RHF reference function were used.

Geometry optimizations

Since it is known from previous work [6] that the hccs can be very sensitive to geometry changes, several levels of approximation were tried for the geometry optimization. This was done for all wave function symmetries, but most systematically for the $^2B_2$ wave function. The results are shown in Table 2 for geometries obtained at the UHF/4-31G, UHF/6-31G*, MP2/6-31G, MP2/6-31G*, and MP2/6-31G** levels. For each geometry, the table summarizes the most important geometrical parameters, the CI energy and the corresponding number of configurations, the SDCI(Q) energy obtained by extrapolation to the full CI(FCI) limit, according to the formula given by Davidson and Silver [12], plus the three different isotropic proton hccs. Results of a UHF/6-31G** geometry optimization are not included in Table 2 since the hccs obtained at this geometry differed from those at the UHF/6-31G* geometry by less than 0.1 G. Likewise, the results of an MP2/4-31G optimization have been omitted, since they differ only marginally from MP2/6-31G.

The expectation value of S^2 was 0.763 in the UHF optimizations and 0.752 in the MP2 optimizations. The deviation from pure doublet symmetry is thus small, especially in the MP2 case, which is usually taken as an indication of good reliability in the geometry optimization.

As shown by Table 2, the geometry has a very strong influence on the hcc values. The value of a_2 changes by more than 30% from the UHF/4-31G to the MP2/6-31G* geometry, reducing the discrepancy with the experimental value of 98 G [3] from 31% to only 8%. The further changes in geometry which were obtained by including p orbitals on the hydrogen atoms can be seen to be small. In this respect, the present system differs from the cations of methane [13] and ethane [14], where polarization functions on the hydrogen atoms have been shown to be essential to predict even a qualitatively correct ground state. The bulk of the present investigation was therefore carried out at the MP2/6-31G*

Table 2. Results for the $^2B_2$ state of the propane cation[a]

	Level of geometry optimization				
	UHF/4-31G[b]	UHF/6-31G*	MP2/6-31G	MP2/6-31G*	MP2/6-31G**
R(C–C)	1.646	1.625	1.620	1.576	1.576
R(C–H_1)	1.075	1.077	1.092	1.088	1.083
R(C–H_2)	1.095	1.097	1.123	1.121	1.114
R(C–H_3)	1.073	1.076	1.091	1.087	1.082
α	112.5	112.3	112.3	112.3	112.4
β	93.9	93.1	92.9	92.1	91.3
γ	112.2	112.1	111.2	110.4	110.8
δ	111.8	112.2	113.4	114.3	114.1
ϕ	96.1	95.9	95.7	94.4	94.4
$\langle S^2 \rangle$	0.7634	0.7633	0.7525	0.7517	0.7517
SDCI energy	−118.31994	−118.32089	−118.31986	−118.31980	−118.32041
No. of conf.	30,023	30,321	30,143	30,293	30,447
SDCI(Q)	−118.44420	−118.44592	−118.44658	−118.44751	−118.44732
a_1(G)	−8.2	−7.8	−7.4	−7.1	−7.1
a_2(G)[c]	68.1	72.8	78.5	90.0	88.6
a_3(G)	−5.8	−5.9	−5.9	−5.7	−5.8

[a] Distances in Å, energies in a.u., angles in degrees, hcc in Gauss. All CI results are for the same [5*s*, 4*p*, 1*d*/4*s*, 3*p*] basis

[b] [4]

[c] [3] gives an experimental value of 98 Gauss

level. For checking purposes, however, the final geometries of all relevant states were recalculated at the MP2/6-31G** level, although the structural parameters and hccs turned out to differ only slightly from the MP2/6-31G* ones.

It can be seen that the most important geometrical effect of electron correlation is to shorten the C–C bonds. This reflects the nature of the $4b_2$ orbital, which is mainly C–C–C bonding (cf. [4]), making about 90% of the spin density concentrated on the carbon atoms. A slight lengthening of the C–H bonds can also be seen, whereas the bond angles are relatively unaffected. One can also observe that inclusion of polarization functions in the geometry optimization gives a rather modest improvement unless electron correlation is considered simultaneously, whereas the combination of both gives a very accurate result. The final result of 89 G for the largest hcc has only a 10% error; errors of this size are usual in high level hcc calculations. As noted above, the hcc is sensitive to molecular geometry, so comparable errors have been introduced by neglect of thermal and zero point vibration.

Stability of the C_{2v} symmetry

In many respects, the propane cation is best regarded as a substituted methane cation. The methane cation is nominally a ^2T state at T_d geometry. Replacement of two protons of the methane cation by methyl groups would split this degenerate ^2T state into $^2A_1$, $^2B_1$, and $^2B_2$ states. Further, CH_4^+ itself is strongly distorted by Jahn–Teller effects into a C_{2v} shape with two long CH bonds (and correspondingly small HCH angle) and two normal CH bonds. Calculations with small basis sets, however, reported an artifactual distortion to a C_{3v} geometry with one long CH bond and three normal ones. As will be discussed below, the propane cation calculations also have this problem. The methane cation has six equivalent minima separated by a small barrier to pseudo-rotation [17]. Perturbation of this potential surface by methyl substitution could still leave it quite flat and complicated.

On the basis of semiempirical and minimal basis *ab initio* calculations, Bellville and Bauld [15] suggested that the propane cation has a lower symmetry than C_{2v} in its ground state, namely a C_s structure with one long and one short C–C bond. Bouma et al. [13] performed a vibrational analysis of the $^2B_2$ ground state at the UHF/3-21G level, and obtained one imaginary frequency with the magnitude 943 cm^{-1}, confirming the saddle point character of this state. They also found a "long-bond" C_s structure of lower energy, similar to the one of Bellville and Bauld. However, the energy difference between the C_{2v} and C_s ground states, calculated by MP3 perturbation theory at the UHF/3-21G geometries, was less than 5 kcal/mol. As the authors themselves point out, this is not a definitive result in view of the inherent inaccuracy of the calculations.

It is, in fact, well established that the UHF approximation artificially favors structures of lower symmetry which give more localized wave functions, whereas higher symmetry and more delocalized wave functions are relatively favored at higher levels of theory which include electron correlation [16]. In order to test if this could be a possible explanation in the present case, we performed CI calculations of the same type as in Table 2 for the long-bond structure obtained at the UHF/4-31G level. The CI energy for the long-bond structure was -118.30275 a.u., which is indeed significantly higher than the C_{2v} energy of -118.31994 a.u. However, this does not prove that the assumption of a long-bond structure is false since a minimum with C_s symmetry could exist somewhere else on the CI potential energy surface.

As a second test, we therefore calculated the vibrational frequencies at two higher levels of approximation, namely MP2/6-31G and MP2/6-31G*. One imaginary frequency was still obtained in the MP2/6-31G calculation, but was now reduced to $195i$ cm^{-1}. In the MP2/6-31G* calculation, however, only real frequencies were obtained, showing that the $^2B_2$ optimum point in C_{2v} symmetry is a true energy minimum. The complete set of harmonic frequencies is given in Table 3. A comparison with the (unscaled) UHF/3-21G results of Bouma et al. [13] shows that the most important difference is in the lowest vibration of b_2 symmetry, which has shifted from $9438i$ to 462 cm^{-1}. This is just the unsymmetrical CC stretch vibration, which shortens one CC bond and lengthens the other one, producing a long-bond structure in the UHF calculations. As for the remaining frequencies, no dramatic changes are seen. Frequencies higher than 1200 cm^{-1} are, on the average, 5% smaller in the MP2/6-31G* calculations than

Table 3. MP2/6-31G* harmonic vibrational frequencies (cm^{-1}) for different states of the propane cation (C_{2v} symmetry)

State	Symmetry	Harmonic frequencies
$^2B_2$	a_1	387, 811, 1153, 1324, 1534, 1545, 2880, 3199, 3225
	b_1	305, 808, 1181, 1324, 3287, 3310
	a_2	133, 967, 1064, 1351, 3303
	b_2	462, 770, 1232, 1334, 1525, 2814, 3215
$^2B_1$	a_1	412, 918, 1074, 1231, 1417, 1542, 2589, 3036, 3243
	b_1	90, 541, 841, 1487, 2258, 3072
	a_2	65*i*, 601, 871, 1435, 3064
	b_2	918, 1004, 1354, 1420, 1508, 3000, 3242
$^2A_1$	a_1	311, 726, 1165, 1246, 1385, 1530, 2940, 3067, 3175
	b_1	859*i*, 181, 971, 1520, 2939, 3197
	a_2	97, 944, 1220, 1504, 3176
	b_2	807, 1040, 1310, 1382, 1898, 3054, 3174

in UHF/3-21G, while the deviations for lower wave numbers are more erratic but still small in most cases.

A third, and perhaps the most conclusive, test of the ground state symmetry is provided by the hccs. As already mentioned, the experimental ESR spectrum in an SF_6 matrix predicts two equivalent protons with an isotropic coupling constant [3] of 98 G. If the ground state were a long-bond C_s structure, a rapid averaging between two equivalent long-bond structures must be assumed (cf. [13]). The proton hccs obtained by such an averaging would, however, be much too small, since they would correspond roughly to an average between the closed shell system $C_2H_5^+$, and a pyramidal methyl radical. In fact, the CI calculation at the UHF/4-31G optimized C_s geometry referred to above predicts a largest average coupling of approximately 20 G, with all others less than 5 G, which evidently disagrees with the ESR results. In contrast, the $C_{2v}(^2B_2)$ result of 89 G agrees well with experiment. In conclusion, a C_s ground state for the propane cation must be ruled out. The potential energy surface around the C_{2v} minimum is, however, undoubtedly quite flat, as shown by the low frequency (133 cm^{-1}) of the lowest a_2 normal mode.

Frequency calculations were also performed at the optimum geometries of the other two wave function symmetries, $^2B_1$ and $^2A_1$. For the geometry obtained from $^2B_1$, only real frequencies were obtained at the UHF/4-31G level. At the MP2/6-31G level, one imaginary frequency of 25*i* cm^{-1} was obtained, which changed to 65*i* cm^{-1} in the MP2/6-31G* calculation. The symmetry of this vibration is a_2 and distortion along this normal mode reduces the symmetry from

C_{2v} to C_2. However, geometry optimizations in C_2 symmetry, starting from a distorted ${}^2B_1$ state, converged to geometries which were very close to the C_{2v} one at both the MP2/6-31G and MP2/6-31G* levels, with identical energies and hccs as for the C_{2v} symmetry, to within the quoted accuracy. Hence, it seems that the small imaginary a_2 frequency in this case does not imply a significant distortion from C_{2v} symmetry. The very low frequency (90 cm^{-1}) of b_1 symmetry should also be noted. Besides being very small, this number would also be expected to be quite sensitive to numerical details of the calculations.

The situation is quite different at the geometry obtained from the C_{2v} constrained ${}^2A_1$ wave function optimization. Here a UHF/6-31G calculation gives two imaginary frequencies at $2019i\ \text{cm}^{-1}(b_2)$ and $423i\ \text{cm}^{-1}(b_1)$. The first of these disappears at the MP2/6-31G level, whereas the second one persists, somewhat increased to $625i\ \text{cm}^{-1}$, a value which is further changed to $859i\ \text{cm}^{-1}$ in the MP2/6-31G* calculation. A distortion along the corresponding normal coordinate (b_1) lowers the symmetry to C_s, with a mirror plane bisecting the C–C–C angle as the only remaining symmetry element. In the reduced symmetry, the ${}^2A_1$ state will obviously transform according to the A' representation. One can note that the same is true for ${}^2B_1$, while ${}^2B_2$ becomes A''.

A geometry optimization in C_s symmetry allows the two C–H bonds in the central methylene group to assume different bond lengths, and also allows all three C–H bonds in the terminal methyl groups to vary independently (the two methyl groups are, however, each other's mirror images). The results of such a C_s constrained geometry optimization is shown in the fourth row of Table 4. This is clearly another "long-bond" structure, but now a CH rather than a CC bond has been elongated. The energy of the ${}^2A'$ stationary point in the reduced symmetry can be seen to be considerably lower than the ${}^2A_1$ stationary point and only 0.3 kcal/mol higher than the ${}^2B_1$ optimum point, but 6–7 kcal/mol higher than the ${}^2B_2$ minimum (this number refers to the MP2/6-31G** energies; the CI energies are less suitable for comparison, on account of differences in number and types of configurations included for the different states).

It should finally be mentioned that the ${}^2A'$ state discussed above does not constitute a true minimum on the energy hypersurface, but rather a saddle point, as indicated by the appearance of one imaginary frequency of $646i\ \text{cm}^{-1}$ in a normal mode analysis. The symmetry of this vibration is a'', breaking the remaining C_s symmetry. With this symmetry restriction removed, a geometry optimization converged spontaneously to the ${}^2B_2$ ground state. Of course, when several local minima are possible, the results of a geometry optimization depends critically on the initial guess.

The ${}^2B_2$ optimum geometry has stretched CC bonds and a decreased CCC angle. Similarly, the ${}^2B_1$ optimum geometry has stretched CH_1 bonds and a decreased H_1CH_1 angle. By analogy with the methane cation, we would expect that there could be four more low-energy regions corresponding to stretching one CH_1 and one CC bond with a corresponding decrease in an H_1CC angle. We have not explored the possibility of this C_1 symmetry structure. Certainly the low energy found for ${}^2A'$ indicates the possibility of such additional minima at lower energy than the ${}^2B_1$ minimum.

Table 4. Isotropic hyperfine coupling constants for the different hydrogen atoms of $C_3H_8^+$, obtained from SD-CI calculations at the MP2/6-31G* optimized geometries[a,b]

State	MP2 energy	Number of Configs.	SDCI energy	SDCI(Q) energy	$a_1(2H)$	$a_2(2H)$	$a_3(4H)$
$^2B_2$	−118.34225	30,447	−118.32041	−118.44732	−7.1	88.6	−5.8
$^2A_1$	−118.32637	30,602	−118.30284	−118.43093	85.8	11.3	24.9
$^2B_1$	−118.33239	31,410	−118.31122	−118.43607	174.01	−0.7	32.1
$^2A'(C_s)$	−118.33188	25,874	−118.26773	−118.44669	279.4	10.2	−2.8(2*H*)
					−7.6		81.5(2*H*)
Experimental SF_6 matrix[b]						98.0	
		$CFCl_2CF_2Cl$ matrix[b]			105.5		52.5
		$CFCl_3$ matrix[b]			100		52
		CF_3CCl_3 matrix[c]			110		50

[a] The geometrical parameters using the same order as in Table 2, are: $^2A_1$: 1.547, 1.101, 1.090, 1.091, 125.2, 113.6, 108.2, 105.8, 129.9; $^2B_1$: 1.471, 1.168, 1.084, 1.095, 62.7, 113.4, 109.8, 109.2, 124.0; $^2A'$: 1.506, 1.161 and 1.083, 1.088, 1.084 and 1.114, 114.3, 113.9, 111.9 and 104.9, 113.8 and 100.8, 124.2

[b] Energy in a.u., hcc in Gauss

Discussion

As mentioned in the Introduction, matrix isolation ESR studies of the propane cation have given different results depending on the matrix used. This has been interpreted in terms of different electronic states of the propane cation in the different matrices, $^2B_2$ in SF_6 and $^2B_1$ or $^2A_1$ in freon matrices [3, 4]. In Table 4 we have summarized our hccs for these three stationary points on the ground state potential surface, obtained from CI calculations including around 30,000 configurations, and performed at the MP2/6-31G** optimized geometries. The MP2 values of $\langle S^2 \rangle$ were less than 0.752 for all states.

In accordance with the previous paragraphs, the assignment of the species observed in the SF_6 matrix to the $^2B_2$ state of the propane cation having C_{2v} symmetry can be regarded as conclusively confirmed. This is also in full agreement with measurements on partially deuterated propane [3], which show that the 98 G couplings are located on the methyl groups and not on the methylene group.

The spectra recorded in the freon matrices, however, still present problems, since neither the $^2B_1$ results of 174 G (2H) and 32 G(4H) nor the $^2A_1$ results of 86 G(2H) and 25 G(4H) fit the reported experimental values of 100–110 G(2H) and 50–52.5 G(4H). In view of the good accuracy obtained in the calculations for the $^2B_2$ state, there is little reason to believe that the CI calculations give much larger errors for the hccs of the two other geometries, which would rule out both of these assignments.

It was, however, shown above that a lowering of the symmetry by removal of one of the symmetry planes of the C_{2v} symmetry group leads to a region on the potential surface with a wave function of $^2A'$ symmetry and an energy 6–7 kcal/mol above the $^2B_2$ minimum. Besides being obtained spontaneously from the $^2A_1$ state when the symmetry is relaxed, this state can be reached from the $^2B_1$ state by the low-frequency (90 cm^{-1})b_1 vibration.

The hccs of the $^2A'$ state given in Table 4 predict a qualitatively incorrect structure for the ESR spectrum due to the use of the wrong number of equivalent nuclei of each type. Further distortion to one of four equivalent ^2A minima in C_1 symmetry, as postulated above, would still not explain the freon matrix ESR spectra. One can, however, note that the calculated (MP2) energy difference between the $^2A'$ stationary point and the $^2B_1$ minimum is small. Assuming that there is a dynamic averaging between the $^2A'$ (or ^2A) structures, a spectrum arising from two equivalent H_1 protons with large couplings and four protons with moderate couplings could be obtained. This would agree with the structure of the observed spectrum. Such averaging is known to occur for methane cation where the ESR hcc for each of the protons is the same.

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