$$d_0 = \frac{OD_\parallel}{OD_\perp} = \frac{F\cos^2\alpha + 0.33(1 - F)}{0.5F\sin^2\alpha + 0.33(1 - F)} \quad (2)$$

To avoid this difficulty, eq 3 following Gangakhedkar et al.[11] can be used

$$d_0 = \frac{OD_\parallel}{OD_\perp} = \frac{2\cos^2\alpha + K}{\sin^2\alpha + K} \quad (3)$$

where K is a stretch-dependent orientation parameter defined by eq 4, where θ is the angle which the molecular orientation axis makes with the stretching direction. Rearranging eq 3, we have

$$K = \frac{2\int_0^{\pi/2} F(\theta)\sin^2\theta\, d\theta}{\int_0^{\pi/2} F(\theta)(2 - 3\sin^2\theta)\, d\theta} \quad (4)$$

$$\cos^2\alpha = \frac{d_0 + K(d_0 - 1)}{d_0 + 2} \quad (5)$$

Integration of eq 4 yields $K = 2$. Substituting this value and $d_0 = 1.8$ for the $S_4 \leftarrow S_0$ band (near uv band) into eq 5 and solving for α, we obtain $\alpha = 18°$. Similarly, α's for $S_1 \leftarrow S_0$ ($d_0 = 0.8$) and $S_3 \leftarrow S_0$ ($d_0 = 1.75$), etc., can be calculated (Table III).

Conclusion

In conclusion, it is suggested that the results of linear dichroism, fluorescence polarization, and relative intensities of the visible vs. "Soret" bands of biliverdin can best be fit to an open, semicircular conformation (e.g., Figure 4). Neither stretched linearly nor fully circular conformations are consistent with the experimental and theoretical analyses described in this report. We further note that the chromophore conformation of phytochrome is likely to be similar to that of biliverdin on the basis of spectral analogies.

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Energetics, Stabilities, and Possible Structures of $CH_5^+(CH_4)_n$ Clusters from Gas Phase Study of Equilibria $CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n$ for n = 1–5

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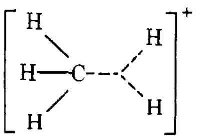
Abstract: The temperature dependence of the equilibria (n − 1,n) $CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n$ was measured in a pulsed electron beam mass spectrometer with a high-pressure ion source for n = 1 to 5. The $-\Delta H$ values obtained were (0,1) 7.4, (1,2) 5.9, (2,3) 4.1, (3,4) 3.9 kcal/mol. The observed enthalpy and free energy changes are compatible with the three-center bond structure for CH_5^+ proposed in the literature. The first two methane molecules interact with the two hydrogen atoms with lowest electron densities forming bridged three-center bonds. Similar structures are also proposed for the higher clusters. An analysis of deviations of the experimental van't Hoff plots permits one to establish the quality of the experimental measurement and the fraction of ions dissociated by the sampling process.

The process $CH_4^+ + CH_4 = CH_5^+ + CH_3$ occurring in electron irradiated methane was among the first ion–molecule reactions observed in mass spectrometers with elevated ion source pressure.[1] However, the existence of protonated methane, protonated ethane $C_2H_7^+$, and attendant ion chemistry in the gas phase observed subsequently in ion–molecule mass spectrometers[2] did not attract wide attention. The few early theoretical calculations on the structure of CH_5^+ used drastically empirical approaches.[3,4] Two more elaborate SCF-MO considered only a limited number[5,6] of structures which later were proved to be of high energy. Strong interest in the CH_5^+ or methonium ion and alkane protonation was created by the work of Olah[7] who investigated protonation of alkanes in super acid (magic acid) liquid solutions. These studies suggested a three-center bond structure I with C_s symmetry. Several theoretical calculations[8-11] have provided independent evidence that this structure is the one with the lowest energy.



I

Some time ago a program of study of ion–solvent molecule interactions in the gas phase was initiated in this labo-

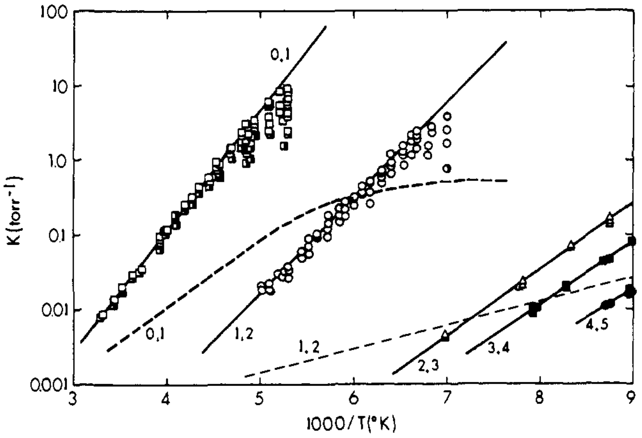


Figure 1. Van't Hoff plots for reactions $CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n$ (n − 1,n): □ (0,1); □ (0,1), CH_4 = 4 Torr; ○ (1,2); △ (2,3); ■ (3,4); ● (4,5); (- - -) plots by Field and Beggs[16] for (0,1) and (1,2).

ratory.[12] The studies are based on measurement of clustering ion equilibria (n − 1,n) in the gas phase where

$$R^+(Sl)_{n-1} + Sl = R^+(Sl)_n \qquad (n - 1,n)$$

R^+ is some ion and Sl some solvent molecule. The temperature dependence of the equilibrium constants $K_{n-1,n}$ leads through van't Hoff plots to $\Delta H°_{n-1,n}$, $\Delta S°_{n-1,n}$, and $\Delta G°_{n-1,n}$. Obviously the $\Delta H_{n-1,n}$ and $\Delta G_{n-1,n}$ relate directly to the binding energies and stabilities of the complexes formed. In some of these studies specific changes of the $\Delta G_{n-1,n}$ and $\Delta H_{n-1,n}$ with n could be related to the structure of the ion R^+. For example a larger drop off in the strength of interaction was observed for $R^+ = NH_4^+$ and the hydrogen bonding solvents NH_3 and H_2O after the fourth solvent molecule.[13] Similar observations relating to the structure of the ion R^+ were made also for other systems like H_3O^+, $CH_3OH_2^+$,[14] and H_3^+.[15] In this connection it appeared of interest to establish whether a specific pattern of interactions, related to the structure of the ion, would be observable in the CH_5^+ system. The most convenient clustering reaction is with CH_4 itself.

$$CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n \qquad (n - 1,n)$$

The binding energies provided by such a study are of thermochemical and theoretical interest in themelves, apart from the information that they might provide on the structure of CH_5^+.

The CH_5^+, methane clustering equilibria, have been studied previously by Field and Beggs.[16] However, these measurements were attended with some experimental difficulties, which reduce confidence in the data obtained. Also, only the (0,1) and (1,2) equilibria were measured, yet one would need at least two or three more steps in order to observe structure in the binding energies.

Experimental Section

The measurements were made with the pulsed electron beam high-pressure ion source mass spectrometer which has been described previously.[17] The reactant gas, in the present case methane, is passed in slow flow through the field free ion source. Short (10 μsec) pulses of electrons produce primary ionization. In methane this leads mostly to CH_4^+ and CH_3^+. The CH_5^+ and $C_2H_5^+$ ions produced by the fast bimolecular processes, $CH_4^+ + CH_4 = CH_5^+ + CH_3$ and $CH_3^+ + CH_4 = C_2H_5^+ + H_2$, can cluster with CH_4. The position of the clustering equilibria depends on the temperature and pressure of the ion source. The reactions of the $C_2H_5^+$ ion will be reported in a separate publication.[18] Some of the ions diffuse to the vicinity of the ion exit leak and escape into an evacuated region where they are magneticaliy mass analyzed and detected. Ion-time dependence profiles are obtained by collecting the ion counts of an ion with given m/e in a multiscaler whose sweep is started by the electron pulse. The ion-time profiles are assumed to represent the ion concentration changes in the ion source. Achievement of equilibrium is assumed to occur when two reactively coupled ions show an ion intensity ratio which is independent of time. The equilibrium constants are then determined with the equation $K_{n-1,n} = I_n/(I_{n-1}P_{CH_4})$ where I_n and I_{n-1} are the observed ion intensities at long reaction times, i.e., after the ratio has become constant.

Impurity ions like $(CH_4HOH_2)^+$ due to the presence of water could be reduced to less than 5% of the total ionization by working with ultra high purity methane which was passed through a trap loaded with 5A molecular sieve and chilled with a Dry Ice-acetone mixture.

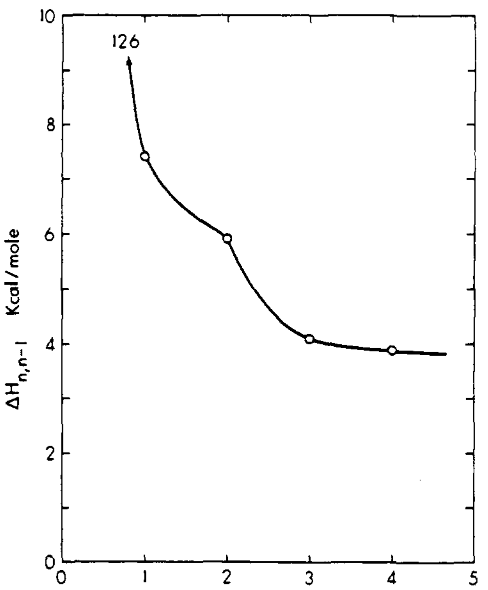


Figure 2. Plot of experimental $\Delta H_{n-1,n}$ vs. n for reactions $CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n$.

Results

Effect of Collisional Dissociation of Clusters Outside Ion Source. The van't Hoff plots for the reactions n − 1,n are given in Figure 1. The $\Delta H_{n-1,n}$ obtained from the slopes of

$$CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n \qquad (n-1,n)$$

the straight lines are shown in Figure 2 as a function of n. The $\Delta H°$, $\Delta S°$, and $\Delta G°$ values are summarized in Table I which also includes the earlier data of Field and Beggs.[16]

In the present work it was observed that under certain conditions, constant temperature plots of the equilibrium quotient $Q_{n-1,n} = I_n/(I_{n-1}P)$ were not constant with methane pressure P, as they should have been for equilibrium conditions where $Q = K$. Instead it was found that for low pressures (P less than approximately 2 Torr) Q was constant with P, but at higher pressures Q decreased with pressure. This effect can be seen in the van't Hoff plots shown in Figure 1. An appreciable downward scatter is observed for the (0,1) and (1,2) plots in the low-temperature region of each plot where I_n/I_{n-1} approaches or exceeds unity. The downward deviation increases with pressure. For the (0,1) equilibrium the highest pressure used was 4 Torr. The 4 Torr points in Figure 1 give the largest negative deviation and do not give a straight line for the region $1/T > 4.5 \times 10^{-3}$. We attribute this effect to collisional dissociation of the clusters outside the ion source which corresponds to an effective conversion of I_n to I_{n-1}. Assuming that a fraction

Table I. Results from Equilibrium Measurements[a]

n,n-1	Reaction	$\Delta H°$, kcal/mol	$\Delta S°$,[b] eu	$\Delta G°$,[c] kcal/mol
1,0	$CH_5^+(CH_4) = CH_5^+ + CH_4$	7.4 ± 0.1 (4.14)[d]	20.8 ± 0.2 (12.4)[d]	1.2 ± 0.1 (0.45)[d]
2,1	$CH_5^+(CH_4)_2 = CH_5^+(CH_4) + CH_4$	5.9 ± 0.1 (1.47)[d]	24.4 ± 0.5 (7.2)[d]	−1.4 ± 0.2 (−0.69)[d]
3,2	$CH_5^+(CH_4)_3 = CH_5^+(CH_4)_2 + CH_4$	4.1 ± 0.1	26.1 ± 0.4	−3.7 ± 0.1
4,3	$CH_5^+(CH_4)_4 = CH_5^+(CH_4)_3 + CH_4$	3.9 ± 0.1	26.6 ± 1.0	−4.1 ± 0.3

[a] Errors given correspond to standard deviation from least-squares treatment of van't Hoff plots. Actual error believed larger, probably around 10–20% of value obtained. [b] Standard state 1 atm. Results given correspond to the temperature of the van't Hoff plot. However, since $\Delta S°$ dependence with temperature is small, $\Delta S°$ values are approximately equal to those at 298°K for reactions (1,0) and (2,1). [c] At 298°K. Standard state 1 atm. Values for high $(n,n-1)$ involve considerable extrapolation of van't Hoff plots obtained at much lower temperatures. [d] Field and Beggs.[16]

α of I_n(true) got converted to I_{n-1} then the observed ion intensities will be $I_n = I_n(\text{true})(1 - \alpha)$ and $I_{n-1} = I_{n-1}(\text{true}) + \alpha I_n(\text{true})$. It is easy to show that in such a case the observed equilibrium coefficient Q will be related to the true equilibrium constant K by eq 1, where

$$PQ = (1 - \alpha)/[(1/PK) + \alpha] \qquad (1)$$

P is the pressure of the clustering gas. It should be noticed that the product PK corresponds to the true (equilibrium) ratio of I_n/I_{n-1} while PQ corresponds to the observed ratio. From the pressure dependence of Q we know that α increases with pressure. However, we expect that α will be approximately independent of temperature. In the high-temperature region of a given plot, $1/PK \gg \alpha$ which leads to $Q = (1 - \alpha)K$. In this region a van't Hoff plot of Q determined at constant pressure will lead to a straight line with the same slope as that for K but displaced downward by log $(1 - \alpha)$. At progressively lower temperatures K increases rapidly and $1/PK$ will begin to become more equal to α. In this region the van't Hoff plot will show curvature and ultimately level off to a horizontal line corresponding to $Q_{\max} = (1 - \alpha)/P\alpha$. This behavior is illustrated in Figure 3 where four van't Hoff plots are shown for a constant pressure of 1 Torr and four different α's. The line corresponding to $\alpha = 0$ (i.e., no instrumental deficiency) was selected to coincide with the straight line of the experimental van't Hoff plot for (0,1) of Figure 1.

Examining the lines with $\alpha \neq 0$ one observes that curvature in the plots occurs earlier the larger the value of α. In an experimental determination with some experimental scatter, portions of the plot showing gentle curvature may be mistaken for straight line regions. This will lead to lines with lower slope and $|\Delta H|$ values that are too low. This is illustrated in Figure 3a for $\alpha = 0.6$ where straight line approximation leads to a $-\Delta H = 6.5$ compared with the $\alpha = 0$ value of $-\Delta H = 7.4$ kcal/mol.

Shown in Figure 3b is a plot of $Q_{0,1}$ calculated from eq 1 for $P = 4$ Torr. The value for α was selected to fit the experimental points at 4 Torr (see Figure 1). A good fit is obtained for $\alpha = 0.1$. The success of the fit lends support to the assumed existence of instrumentally induced conversion of I_n to I_{n-1}. We believe that collisional dissociation of I_n to I_{n-1} occurs in the region immediately outside the ion exit slit, where the gas pressure is highest. Since the binding energies of the clusters are low, less than 10 kcal/mol, in the present case, collisions of ions, accelerated by only 1 V, with gas molecules can lead to cluster dissociation. The newly created lower mass cluster I_{n-1} will be detected at the mass corresponding to I_{n-1}. In general the mass shift (in a magnetic mass spectrometer) caused by the somewhat lower effective accelerating voltage experienced by the collision created I_{n-1} ion will be too small to be noticed, particularly in the presence of normal I_{n-1} ions. One expects that the cross sections for such dissociations will increase as n increases because the clusters get larger and the bonding weaker. Therefore an effective conversion of I_n to I_{n-1} can occur also if both ions dissociate in part to clusters lower than $(n - 1)$ but I_n does so with a larger cross section.

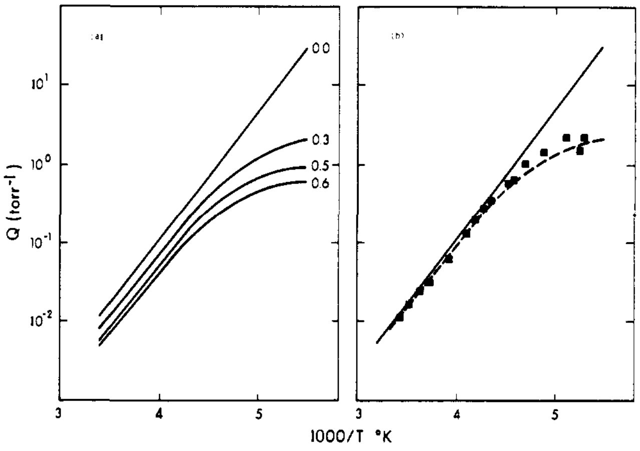


Figure 3. (a) Effect of instrumentally caused collisional dissociation converting higher cluster I_n to I_{n-1} on van't Hoff plots. Numbers beside curves give the value for α which corresponds to the fraction of I_n converted to I_{n-1}. $Q = I_n/(I_{n-1}P)$ where I_n, I_{n-1} are experimentally observed ion intensities. For $\alpha = 0$, Q equals the equilibrium constant. Calculations for constant pressure 1 Torr. (b) Comparison between equilibrium constant without collisional dissociation ($\alpha = 0$) and experimental points for Q obtained at 4 Torr. Dashed line represents fit to experimental curve using eq 1 and $\alpha = 0.1$.

We have been long aware of the occurrence of collision induced dissociation in ion sampling,[19] and have generally worked with narrow ion exit slits and gas pressures such that molecular flow conditions prevail in the ion exit slit. The result for 4 Torr, Figure 3b, indicating that some 10% of $CH_5^+(CH_4)$ dissociate to CH_5^+ is not unreasonable for an ion exit slit of 15 × 1000 μ. In earlier work[19,20] with different reaction systems we did observe that the curvature of van't Hoff plots obtained at high pressure could be removed through the use of a narrower ion exit slit. The results in Figure 3 show that it is advantageous to work under conditions where the $PQ < 1$ since the error due to dissociation has then a minimal effect on the van't Hoff slope.

It should be pointed out that deliberate extension of the experiments to high values of PQ until curvature in the plot appears can be used as a diagnostic test of the suitability of the sampling system and determination of the probable degree of dissociation α.

We wish also to draw attention to the fact that incomplete equilibration due to insufficient reaction time will lead to an equation identical with (1). In that case α will be the fraction of I_n left unconverted and still present as I_{n-1} because of incomplete achievement of equilibrium. Thus work at low PQ values also would partially alleviate problems arising from incomplete equilibration.

The results of Field and Beggs[16] for the (0,1) and (1,2) equilibria included in Figure 1 and Table I are seen to be in disagreement with the present work. The van't Hoff plot for the (0,1) equilibrium (Figure 1) taken at constant pressure of 1 Torr[16] shows appreciable curvature. In view of the discussion above one may suspect that this is caused at least in part by collisional dissociation outside the ion source with a dissociating fraction α which is larger than 0.6 (see Figure

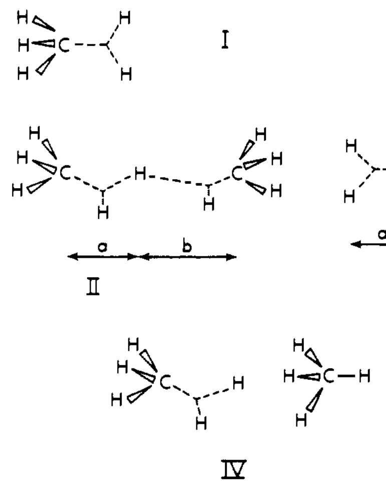


Figure 4. Structures of clusters. I: CH_5^+ with three-center bond and C_s symmetry. II: $CH_5^+{\cdot}CH_4$. One of the electron deficient H atoms interacts with the electron pair of a C–H bond in the CH_4 molecule. III: predicted structure for H_5^+ by theoretical calculations. Axis of H_2 is rotated by 90° with respect to the H_3^+ plane. IV: another possible structure for $CH_5^+{\cdot}CH_4$. Electron deficient H atom of CH_5^+ molecule interacts with three C–H bonds of the CH_4 molecule.

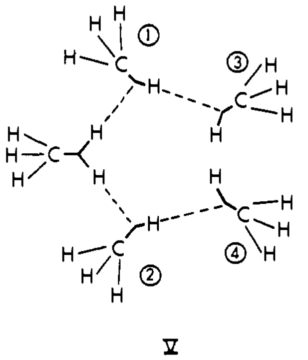


Figure 5. Structure V: three-center bond structure for $CH_5^+(CH_4)_2(CH_4)_2$. Molecules 1 and 2 form weak three-center bonds with acidic hydrogens of CH_5^+. Molecules 3 and 4 form weaker three-center bonds with acidic hydrogens in molecules 1 and 2.

3a). The larger slit width and the restricted pumping geometry in the ion exit region of the instrument used[16,20] is compatible with such a large α. A reason of different nature has been suggested by Field[16,21] for the observed curvature of the van't Hoff plots at low temperature.

It appears that the large discrepancy with the Field (1,2) plot (Figure 1) cannot be explained only on the basis of the presence of appreciable dissociation in the ion sampling process. It might be significant that Field and Beggs[16] did have to increase the repeller voltage as they decreased the temperature. In later work with the same instrument[22] it was found that higher repeller fields did decrease the equilibrium quotient and corrections were applied to obtain an equilibrium constant. No such corrections seem to have been made in the CH_5^+ clustering[16] work. It is also possible that ion source temperature inhomogeneities at low temperatures might have been present because of the proximity of the electron filament to the ion source on the apparatus used.[16]

The entropy changes obtained by Field and Beggs[16] can be shown to be too low. The translational entropy change for the 1,2 reaction accurately evaluated by the Sackur Tetrode equation amounts to −33.1 eu. Since $\Delta S_{\text{rot}} \approx 0$ Field's $\Delta S^\circ_{1,2} = -7.2$ eu would require a ΔS_{vib} of 26 eu. Since the association leads to appearance of only a few vibrational degrees of freedom such a large vibrational entropy change is inconceivable.

Relationship of Cluster Dissociation Energies $\Delta H_{n,n-1}$ to Structures of Clusters $CH_5^+(CH_4)_n$ and the Structure of CH_5^+. The measured enthalpy changes for the $(n-1,n)$ reactions are shown in Figure 2 as a function of n. A decrease of $\Delta H_{n,n-1}$ ($\Delta H_{n,n-1} = -\Delta H_{n-1,n}$) with n is observed as is always the case for ion clusters. The decrease is expected because of gradual charge dispersal with the addition of new clustering molecules. The results of Figure 2 show that this decrease is not regular. The fall-off between the first two interactions $\Delta H_{1,0}$ and $\Delta H_{2,1}$ is somewhat smaller; then an appreciable decrease occurs between $\Delta H_{2,1}$ and $\Delta H_{3,2}$ followed by only a small decrease to $\Delta H_{4,3}$. A very similar pattern can be observed directly in the van't Hoff plots shown in Figure 1. The vertical distance between two adjacent van't Hoff plots taken at some constant $(1/T)$ corresponds to $(\Delta G^\circ_{n+1,n} - \Delta G^\circ_{n,n-1})(1/2.3RT)$ and is thus proportional to the free energy differences. Big gaps between two van't Hoff plots thus indicate a big drop of stability toward dissociation of one molecule. Easily noticed by inspection of Figure 1 is the big gap between the plots (1,2) and (2,3) and the two little gaps between (2,3), (3,4) and (3,4), (4,5). Thus the first two incoming CH_4 molecules interact relatively strongly while the next three molecules experience weaker and quite similar interactions.

This pattern of interactions is consistent with the proposed three-center bond structure of the CH_5^+ molecule of C_s symmetry. The two H atoms participating in the three-center bond have the lowest electron density, i.e., the highest positive charge or the highest acidity. Attachment of two CH_4 molecules to these H atoms leads to the first two, stronger interactions. The remaining three CH_4 molecules then attach more weakly. This pattern of interactions is also compatible with the D_{3h} structure for CH_5^+ which consists of a planar CH_3 group with one H atom above and one below the CH_3 plane and in which these two atoms have lower electron density.[8-11] However, this structure has an energy that is higher by some 14 kcal/mol[11] than the three-center bond C_s structure. Conversion to this structure induced by the clustering can also be excluded since then the observed pattern of energy changes would have been different.

The nature of the bonding involved between CH_5^+ and CH_4 in the $CH_5^+CH_4$ species is of some interest. A two three-center bond structure II is shown in Figure 4. An analogy can be made between $CH_5^+{\cdot}CH_4$ and $H_3^+H_2$. The experimentally determined[15] $\Delta H_{1,0}$ for the $H_3^+{\cdot}H_2$ system was found equal to 9.6 kcal/mol. This is somewhat higher but still close to $\Delta H_{1,0} = 7.4$ kcal/mol for $CH_5^+{\cdot}CH_4$ found in the present work. The structure of H_5^+ has been examined theoretically by several workers (Poshusta[23] and references therein). The calculations agree on a structure with C_{2v} symmetry corresponding to III in Figure 4 in which the two hydrogen atoms on the right are twisted 90° out of the plane of the H_3. The distance b (Figure 4) is found to be considerably larger than the distance a. Thus the H_5^+ consists essentially of a distorted H_3^+ which interacts through one of its atoms with the electron pair of an H_2 molecule. Assuming that the situation in $CH_5^+{\cdot}CH_4$ is similar one can propose the bridged two three-center bond structure II (Figure 4).

Considering that the distance b (structure II) is probably larger than 3 Å, a specific interaction with one of the C–H bonds of the methane molecule might not be involved but rather an interaction with three C–H bonds as indicated in structure IV, Figure 4.

The further buildup of the cluster depends on whether structure II or IV is more stable. Starting with structure II one might expect that the next two CH_4 molecules would go not to the H atoms at the back of the CH_5^+ molecule but to the acidic protons of the two CH_4 molecules engaged in the three-center bonds. The resulting structure V is shown in Figure 5. The next, i.e., fifth, molecule must go then to an "outer" position compared with the positions available for the third and fourth molecule, and have a weaker binding energy. The van't Hoff plots (Figure 1) are compatible with such a situation. If the third, fourth, and fifth molecules went to similar positions one would have observed small and gradually decreasing gaps between the van't Hoff plots for the (2,3), (3,4), and (4,5) equilibria. Examining Figure 1 one finds that the gap between (3,4) and (4,5) is actually bigger than the gap between (2,3) and (3,4). This could mean that the fifth molecule goes to a different and less favorable position and is in agreement with the buildup of structure II to structure V (Figures 4 and 5) and beyond.

Assuming that the more favorable structure for $CH_5^+\cdot CH_4$ is given by IV one would expect that the second molecule will go opposite the second acidic hydrogen of the three-center bond in CH_5^+, but that the third, fourth, and fifth molecule would go opposite the three remaining H atoms of the CH_5^+. This would mean three similar and gradually decreasing interactions and be actually incompatible with the somewhat larger (3,4) to (4,5) gaps in the van't Hoff plots discussed above, unless one invoked special steric hindrance for the incoming fifth molecule.

Structures as complicated as V or the alternative considered above cannot be established on the basis of energetics data alone. Therefore, it would not be profitable to speculate further. However, we think that the structures of the protonated methane clusters are interesting and that they might also be useful in considerations of the state of the proton in liquid hydrocarbon solutions.

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A Quantum Mechanical Approach to Conformational Analysis

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Abstract: The classic bulk approach to conformational preference in organic chemistry is shown to be less satisfactory than an approach which considers the energy components T, V_{ne}, V_{ee}, and V_{nn}. The attractive steric effect is shown to have its origin in the dominance of ΔV_{ne} over $\Delta V_{ee} + \Delta V_{nn}$. This is demonstrated through consideration of several ab initio SCF calculations. These include the methyl and ethyl rotations of *n*-butane; the conversion of chair cyclohexane to the twist-boat and boat conformations; and the axial vs. equatorial preference of methyl and fluoro substituted chair cyclohexanes. Moreover, the attractive steric effect is found to be crucial for a proper understanding of the gauche-anti reaction coordinate, and it can be important in cis and trans alkenes. Axial preference in chair cyclohexanes is caused by dominance of the ΔV_{ne} term.

Historically, discussions of steric and conformational effects have emphasized the repulsive terms arising from interactions between nonbonded atoms or groups. Such approaches assume that bringing two large nonbonded groups into closer proximity leads to unfavorable interactions. Thus, groups of greater "bulk" or "size" tend to be equatorial in cyclohexanes, anti in 1,2-disubstituted ethanes, or trans in alkenes with respect to other bulky groups.[1] However, this bulk approach to steric or conformational effects is unsatisfactory on two counts. First, it is often wrong; numerous examples are known where the system is actually more stable with the large groups closer. Axial preference can be found,[2] some disubstituted alkenes are more stable in the cis form,[3-5] and 1-chloro- and 1-bromopropane prefer the gauche conformation.[6] Second, this bulk approach is not quantitative and gives no real measure of the strength of the interaction between the groups. Moreover, in some cases where the bulk approach gives qualitatively correct predictions, the dominant interactions are really attractive rather than repulsive.