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Structure and Vibrational Analysis of Protonated Ethane $C_2H_7^+$#

Shigeki OBATA and Kimihiko HIRAO*,†
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01
†Department of Chemistry, College of General Education, Nagoya University, Nagoya 464-01

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The stability and vibrational frequencies of protonated ethane, $C_2H_7^+$, have been studied by *ab initio* molecular orbital theory. The IR spectra for $C_2H_7^+$ recorded by Y. T. Lee's group## were interpreted from a theoretical point of view. *Ab initio* computations predict the existence of two isomers, a bridged structure, and a tight and loose open form. The loose open form is represented as an H_2 molecule attached loosely to a classical open $C_2H_5^+$ ion. The different behavior observed in the IR spectra can be attributed to the changing ratio of the bridged $C_2H_7^+$ to the open $C_2H_5^+$ isomers. The final interpretation of these data is that the spectrum at 150 Torr (1 Torr=133.322 Pa) arises from the bridged structure which is the most stable form of $C_2H_7^+$. The additional band in the spectrum observed at 60 Torr originates form the weakly bound complex which dissociates upon absorbing a single IR photon.

Carbocations are well known to play an important role as highly reactive intermediates in organic reactions. In addition, astrophysical interest in carbocations has increased in recent years.[1—3] They can have two possible structures, a classical open structure and a non-classical bridged structure. Many ions are detectable by experimental techniques such as mass spectroscopy and some information on their heat of formation may be available.[4—20] However, little information about their detailed structures is known from experiments. Recently a variety of other experimental methods have been applied to the study of molecular ions. Notably, the microwave technique[21] and IR spectra[22] give quantitative data about geometries of these ions.

In contrast, theoretical work on carbocations has been extensive.[23—41] Structures for singlet carbocations with up to three carbon atoms have been the subject of several recent theoretical investigations. These works have dealt with the classical and non-classical structures.

Early *ab initio* calculations on small carbocations were performed with the minimal and double-zeta basis sets at the SCF level.[23—30] It was soon recognized, however, that such simple levels often failed in describing relative energies and that the addition of polarization functions to the carbon basis sets preferentially stabilizes the bridged structures relative to the classical ones.[31,32] It was also found that inclusion of electron correlation favors the non-classical bridged structures.

For protonated methane, CH_5^+, the most stable isomer is a C_s form with a three-center bond involving CH_3 and two hydrogen atoms.[33,36,39—41] This is more stable than the trigonal bipyramid form (D_{3h}). The methyl cation is predicted to be planner. The lowest vacant molecular orbital of CH_3^+ is a carbon 2p function orthogonal to the molecular plane. Thus we would expect CH_3^+ to participate head-on in the donor–acceptor complex with the area rich in electron density. In the C_s form, the hydrogen molecule acts as an electron source and withdrawal of electrons from σ bonding orbital of a hydrogen molecule leads to lengthening of the H–H distance. Another stable isomer is a C_{2v} form. In this case, the methane is an electron donor and the proton is an electron acceptor. Charge transfer (CT) occurs from one of the degenerate HOMO of the methane to the proton. The separation of the energies of the C_s from the D_{3h} form increases markedly if polarization functions are added to the basis functions. Our previous study[39] including correlation correction still indicates the C_s form to be the most stable, although the C_{2v} lies only 0.7 kcal mol^{-1} above it. This proximity implies a low activation barrier for interchange or scrambling of the hydrogen nuclei.

Protonated acetylene, $C_2H_3^+$ could exist either as a classical structure or as a non-classical bridged structure.[29,31,34—36,38—40] Early work[25] on these structures at the SCF level without polarization functions indicated that the classical structure was substantially more stable than the bridged structure. However, the addition of d functions sharply lowers the energy difference.[29] The correlation energy is considerably greater in the bridged structure than in the classical. A final prediction is that the non-classical bridged structure is the most stable.[31] Taking into account the electron correlation and the polarization effects, Ragharachari et al. concluded that the bridged structure is more stable than the classical by 3.0 kcal mol^{-1}.[38] According to a recent study, the energy gap between the classical and bridged is 1.3 kcal mol^{-1}.[39]

Protonated ethylene, $C_2H_5^+$, also has possible classical and non-classical structures. Early work by Pople's group indicated that the classical structure is more stable.[25] A full study including the addition of the polarization functions reduces the gap substantially. Again, addition of correlation effects favors the bridged form.[29,31]

#This paper is dedicated to the late Professor Hiroshi Kato.

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Protonated ethane, $C_2H_7^+$ is similarly believed to have two isomeric structures, classical open and nonclassical bridged form. The bridged structure corresponds to protonation in the center of the C–C bond. The open structure is a complex between the classical $C_2H_5^+$ and an H_2. Table 1 lists the relative energies obtained in the previous calculations. The table shows that the most stable structure is the bridged one. Clearly, the energy gap is reduced as the calculation is improved in either dimension, basis set, and wavefunction. The table also includes the distance between the classical $C_2H_5^+$ ion and the H_2 molecule in the open structure. Basis sets with DZ and/or DZ plus d functions give a weak complex between the classical $C_2H_5^+$ and H_2 with the distance of 2.7 Å. Optimization of the geometry with DZ plus d and p functions and/or with inclusion of correlation corrections change the picture dramatically. Refinement of the theory gives the tight complex of the classical $C_2H_5^+$ and H_2. The distance of $C_2H_5^+\cdots H_2$ is shortened into 1.2 Å and the energy gap is reduced to 4.3 kcal mol^{-1}. It is of interest that significant binding of the $C_2H_5^+$ and H_2 fragments does not occur until the correlation effect is included in the theory.

Experimentally $C_2H_7^+$ has been observed with high-pressure mass spectrometric studies since the 1960's.[4—12] French and Kebarle studied the pyrolysis of $C_2H_7^+$ and determined an activation energy of 10.5 kcal mol^{-1} for dissociation into the most stable $C_2H_5^+$ and H_2.[13] In 1976 Hiraoka and Kebarle claimed to observe both isomers of $C_2H_7^+$.[14—16] They obtained different van't Hoff plots at high and low temepratures. The relative energy between two isomers is 7.8 kcal mol^{-1}. In 1981 Bohme et al. reported the thermodynamic information derived from the rate and equilibrium constant measurements at 298 K.[18] However, until recently no clear quantitative information on the structure for $C_2H_7^+$ was available.

Recently, the IR spectra of protonated ethane in the gas-phase have been recorded with a powerful spectroscopic technique developed by Y. T. Lee's group at Berkeley.[22] An outline of this system is as follows. Parent ions are formed in a corona discharge and then mass-selected. While these ions are caught in an octupole radio-frequency ion trap, they are exposed by a tunable IR laser and excited vibrationally. The spectroscopic probe is carried out with a two color laser scheme. The first laser tunably sweeps from 2500 to 4200 cm^{-1} and excites C–H stretching vibrations. The second laser is CO_2 laser that selectively induces dissociation of the vibrationally excited parent ions through a multiphoton process. The intensity of the photodissociated $C_2H_5^+$ fragment is monitored with a quadrupole mass filter.

Table 1. *Ab initio* Results for the Relative Energies E(classical)$-E$(bridged) of $C_2H_7^+$

[kcal mol^{-1}]

Type of wave function	Basis set			
	MSB	DZ	DZ+d	DZ+d+p
SCF	−10.9[a] (2.7)[e]	−10.6[a] (2.7)	10.1, 9.1[b] (2.7)	8.5[c], 6.7[d] (1.2)
Beyond SCF			6.8[b] (1.3)	6.8,[c] 4.3[d] (1.2)

a) Ref. 23. b) Ref. 38. c) Ref. 36. d) Ref. 39.
e) Values in parentheses are distances between the classical $C_2H_5^+$ and the H_2 in Å.

With this system, they observed two sets of spectral features. The spectra showed different dependence on the backing pressure behind the nozzle in the ion source, on the mixing ratio of C_2H_6 to H_2, and on the presence/absence of the second CO_2 laser.

The spectra at 60, 90, and 150 Torr (1 Torr=133.322 Pa) are shown in Fig. 1. The spectra change dramatically as a function of the backing pressure. The five features at 2521, 2601, 2683, 2762, and 2825 cm^{-1} can be made to disappear by raising the backing pressure, while the higher frequency features at 2945, 3082, and 3128 cm^{-1} almost remain unaffected. An additional band at 3964 cm^{-1} is also found to be dependent on the source conditions used. These features showed the same behavior on increasing the mixing ratio of C_2H_6 to H_2. The obvious question from the observed spectra is why there seems to be two sets of peaks based on backing pressure dependence. Two reasons may be offered. One comes from the hot band hypothesis and the other is the existence of two isomers. According to the discussion by Lee's group, the former seems unlikely. In our previous work,[39] the classical structure is higher in energy than the bridged by 4.3 kcal mol^{-1}. At the higher pressure or mixing ratios, more collisions will occur in the ion source, which leads to more efficient internal cooling of nascent ions. This strongly enhances formation of the lower energy bridged structure over the classical structure.

Additionally, blocking the CO_2 laser makes the features at 2945, 3082, and 3128 cm^{-1} disappear, while the peaks at 2521, 2601, 2683, 2762, and 2825 cm^{-1} remain unaffected. This means that some of the parent ions had been already dissociated without the CO_2 laser. This is also explained by the presence of two isomers. Two color laser scheme is necessary to dissociate the more stable bridged structure.

Thus, the six features at 2521, 2601, 2683, 2825, and 3964 cm^{-1} seem to arise from the classical structure and the three features at 2945, 3082, and 3128 cm^{-1} from the bridged. Lee's group compared the observed frequencies with the theoretical predictions calculated by Dupuis.[22] However, there exists serious conflict between theory and experiment.

To interpret these spectra, we have carried out *ab initio* calculations on protonated ethane. In Sect. 1, struc-

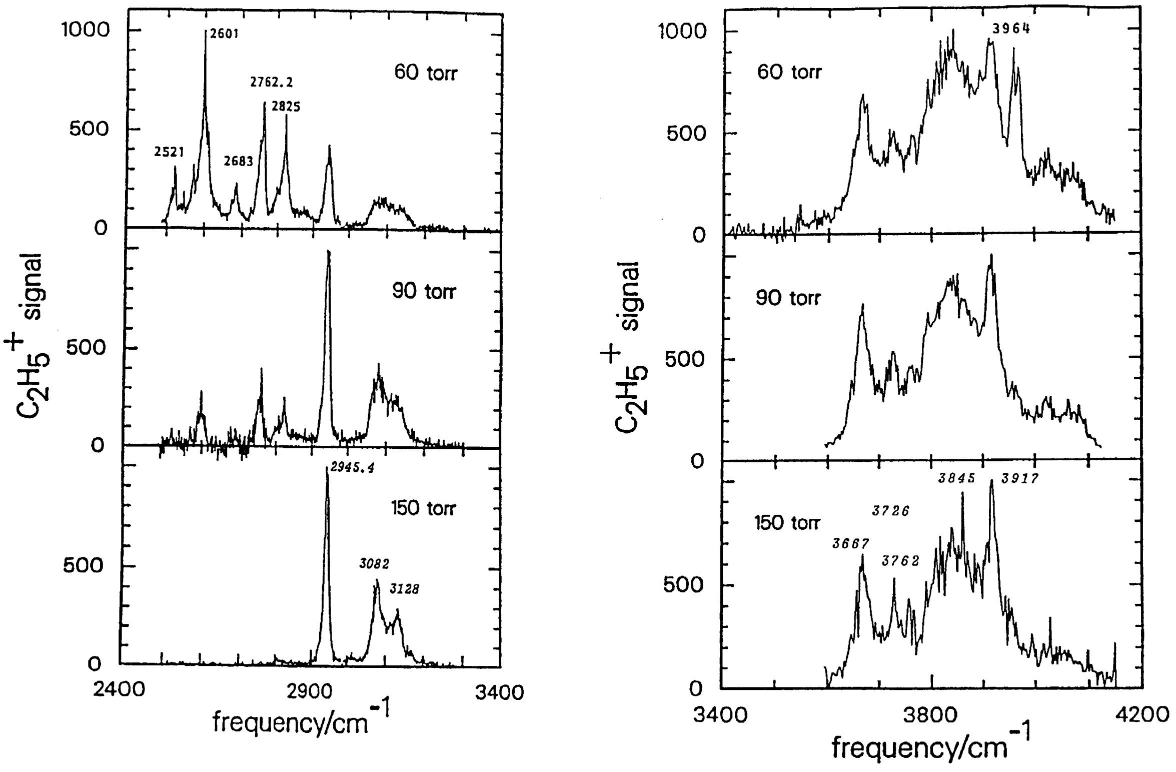


Fig. 1. IR sepctra at 60, 90, and 150 Torr of $C_2H_7^+$ obtained by Yen et al.[22]

tures and stability of $C_2H_7^+$ are discussed. Interpretation of the IR spectra is given in Sect. 2. Conclusions are presented in the final section.

1. Structures and Stability of $C_2H_7^+$

The basis set employed was triple zeta quality augmented by polarization functions. We used Huzinaga-Dunning's [5s3p] and two d functions with an orbital exponent of $\alpha_d=1.368$ and 0.540 for C. For H, [3s] with p functions ($\alpha_p=1.0$) were chosen.[42,43] Optimized geometries, harmonic vibrational frequencies, and intensities at the SCF level were obtained with an analytical derivative technique as implemented in HONDO7.[44] Electron correlation effects were included by the SD-(Q)CI calculations. A core of two shells was kept frozen. The contributions of unlinked quadruple excitations were estimated by the Davidson's correction.

First, we computed geometrical and vibrational parameters for ethane. The optimized geometry of ethane is shown in Fig. 2. The SCF method with a triple zeta plus polarization basis set gives reasonable accuracy in the equilibrium bond lengths and angles. The computational error is believed to be less than 0.02 Å for bond lengths and 2° for bond angles.

The optimized geometries of the bridged and open structures are shown in Figs. 3 and 4, respectively. Total energies are given in Table 2 and the energy diagram is shown in Fig. 5. At all levels of the theory, the bridged structure is lower in energy than the open structure.

For the bridged structure, there are two stationary points on the potential energy surface. Vibrational analysis at the SCF level confirmed that the C_2 form corresponds to a minimum point on the potential surface, while the C_{2v} form is the transition state with respect to a twisting vibration of the C_2 form. The energy difference is only 0.73 kcal mol^{-1} at the SCF level.

These two forms resemble a complex between a methyl cation and methane. For the C–H linkages in the methyl groups, bond lengths and angles are almost the same as those in an isolated methane. The proton, inserted directly into the center of the two methyl groups, behaves as an electron acceptor. The C_2 and C_{2v} forms deviate strongly from the D_{3h} form in which the proton lies in the center of the C–C axis. The central angle CHC is 115.3° in C_2 and is 116.6° in the C_{2v} form. The difference between these forms is the distortion of the methyl groups. In the C_2 form, two methyl groups are

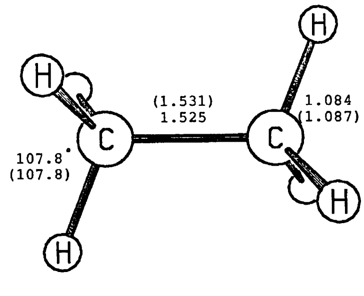


Fig. 2. Opeimized geometry of ethane. Values in parentheses are experimental data. Bond lengths and angles are in Å and degrees.

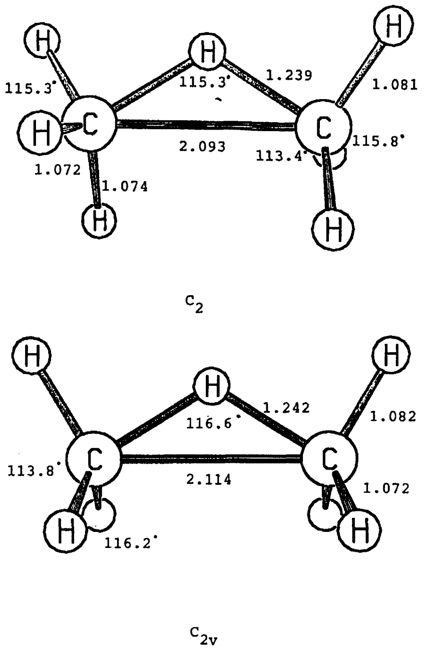


Fig. 3. Optimized geometries of the bridged $C_2H_7^+$ (C_2) and (C_{2v}). Bond lengths and angles are in Å and degrees.

twisted by 56.3° along the C–C axis, and the C–C distance is shorter by 0.02 Å than that in the C_{2v} form. These forms are similar to the C_{2v} protonated methane.

Although the electron correlation favors the C_{2v} form, the shallowness of the potential in the direction of the C_{2v} form allows zero-point vibrational energy correction (ZPE) to displace the minimum. The final prediction with the optimized geometries at the SCF level is that the C_{2v} bridged form is the most stable.

Hiraoka et al. have measured the dissociation energy of $C_2H_7^+$ into the most stable bridged $C_2H_5^+$ ion and an H_2 molecule.[16] The measured value of the bridged structure is 11.8 kcal mol^{-1}. The corresponding values at the SD(Q)CI+ZPE level are 9.9 and 11.1 kcal mol^{-1} for C_2 and C_{2v} forms, respectively. The prediction is in good agreement with experiment.

For the open structure, there exist two stable forms with C_s symmetry. One is the tight open form (A in Fig. 4) and the other is the loose open form (B in Fig. 4).

The tight open form closely resembles a complex involving a classical ethyl cation with a hydrogen molecule. The H–H distance of 0.833 Å is longer than that of 0.734 Å in a free H_2 molecule that is calculated at the same level of the theory. Charge transfer (CT) from the σ bonding orbital of the H_2 molecule elongates the H–H linkage. The other C–H bond distances are similar to those in ethane. The calculated C–C bond length is 1.515 Å. This is slightly shorter than that in ethane (1.525 Å) and much longer than that in the classical $C_2H_5^+$ ion (1.415 Å). The distance between the $C_2H_5^+$ fragment and the H_2 subunit is only 1.3 Å. Thus, this is the tight complex with the two-electron three-center bond involving CHH.

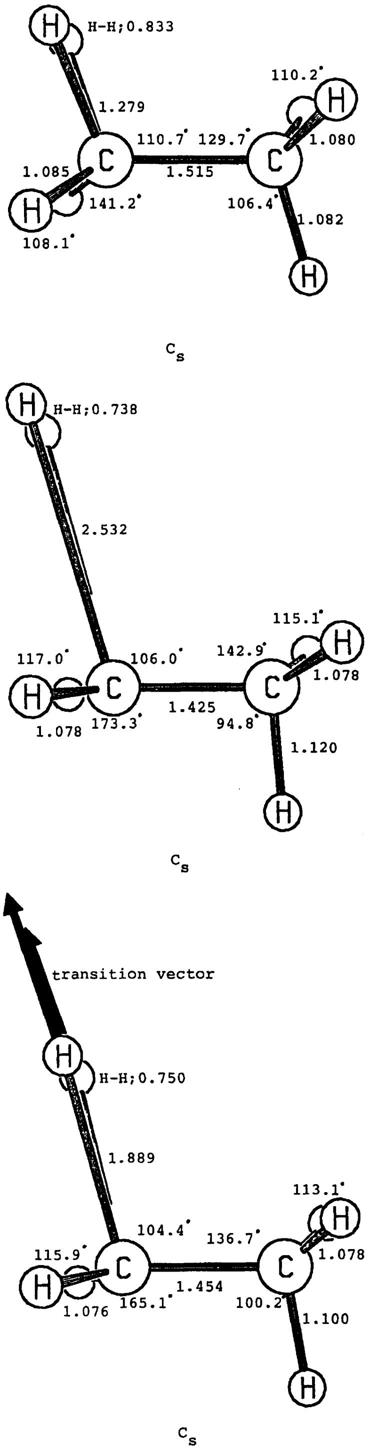


Fig. 4. Optimized geometries of the tight open $C_2H_7^+$ (A) and the loose open $C_2H_7^+$ (B), and the transition state geometry connecting the tight and loose open $C_2H_7^+$ (C). Bond lengths and angles are in Å and degrees. Transition vector in (C) is 245i cm^{-1}.

The tight open form is not a classical but a non-classical structure and it is also very similar to the most stable CH_5^+ ion with C_s symmetry. The terms, classical and non-classical, are widely used to classify carboca-

Table 2. Calculated Total Energies for $C_2H_7^+$

[hartree]

Cations	SCF	SD(Q)CI	SD(Q)CI+DZP
$C_2H_5^+ + H_2$			
Open	−79.474621	−79.823635(−0.349014)[a]	−79.758811(0.0677367)[b]
Bridged	−79.475383	−79.830033(−0.354650)	−79.763833(0.0662001)
$C_2H_7^+$			
Tight open	−79.480271	−79.845442(−0.365171)	−79.769064(0.0763784)
Loose open	−79.476686	−79.826551(−0.349865)	−79.761796(0.0647548)
Bridged (C_2)	−79.494055	−79.856601(−0.362546)	−79.779579(0.0770223)
Bridged (C_{2v})	−79.492890	−79.855254(−0.362364)	−79.781461(0.0737939)

a) Recovered correlation energies. b) Zero-point energies.

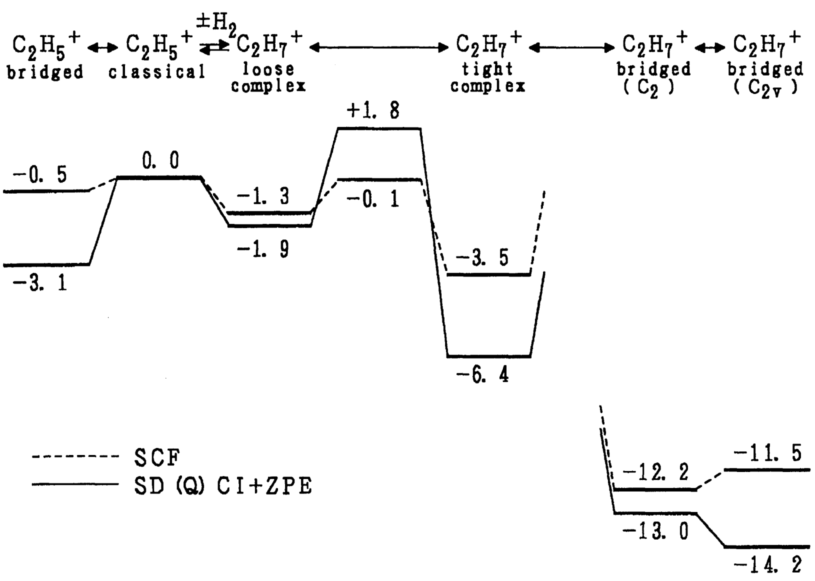


Fig. 5. Theoretical energy diagram of $C_2H_7^+$. Units are kcal mol^{-1}.

Table 3. Comparison of Geometric Parameters of Related Species

Geometric prameters[a]	C_2H_6	Tight $C_2H_7^+$	Loose $C_2H_7^+$	Classical $C_2H_5^+$	C_2H_4	H_2
Bond lengths						
R(C–C)	1.525	1.515	1.425	1.415	1.314	
R(C–Ha)	1.084	1.082	1.120	1.130		
R(C–Hb)	1.084	1.080	1.078	1.078	1.074	
R(C–Hc)	1.084	1.085	1.078	1.079	1.074	
R(C–Hd)		1.279	2.532			
R(Hd–Hd)		0.833	0.738			0.734
Angles						
∠C–C–Hd	111.2	106.4	94.8			
∠Hb–C–Hb)	107.8	110.2	115.1	115.0	115.5	
∠Hc–C–Hc)	107.8	108.1	117.0	117.2	115.5	
∠C–(HbCHb)[b]	127.7	129.7	142.9	146.5	180.0	
∠C–(HcCHc)	127.7	141.2	173.3	174.3	180.0	
∠C–(HdCHd)	110.7	106.0				

a) Bond length in Å and angles in degrees. See Fig. 6 for the corresponding structure. b) Bisector angle.

tions. However it is not appropriate to use the term classical for saturated carbocations such as CH_5^+ and $C_2H_7^+$. They are all non-classical molecules involving a three-center bond.

The loose open form with C_s symmetry is a weakly bound complex between the classical $C_2H_5^+$ and an H_2 molecule. A normal mode vibrational analysis confirmed that the loose open form corresponds to a true

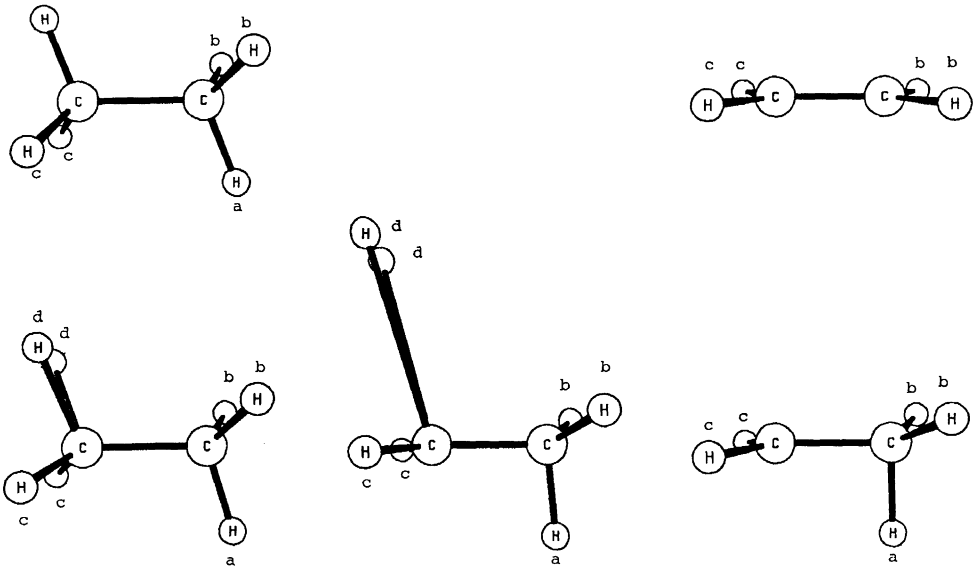
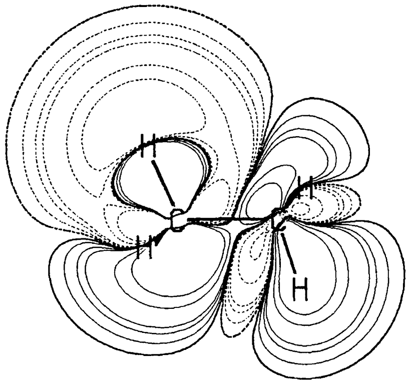
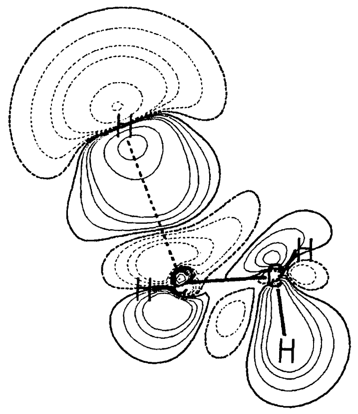


Fig. 6. Comparison of geometries for the loose open $C_2H_7^+$, tight open $C_2H_7^+$ and other relational species.



The Tight Open $C_2H_7^+$



The Loose Open $C_2H_7^+$

Fig. 7. Density difference contour maps for the tight and loose open $C_2H_7^+$.

Table 4. Proton Affinities for Three $C_2H_7^+$ Structures

[kcal mol^{-1}]

Complex	Calcd	Exptl
$C_2H_6+H^+$=bridged $C_2H_7^+$ (C_{2v})	143.4	139.6,[a], 142.1[b]
$C_2H_6+H^+$=bridged $C_2H_7^+$ (C_2)	142.2	
$C_2H_6+H^+$=tight $C_2H_7^+$ (C_s)	135.6	131.6[a]
$C_2H_6+H^+$=loose $C_2H_7^+$ (C_s)	131.1	127.0[c]

a) Ref. 16. b) Ref. 17. c) Ref. 10.

minimum point on the potential surface. A comparison of geometric parameters of these complexes with those of ethane, the classical $C_2H_5^+$, and ethylene are given in Table 3. In the loose open $C_2H_7^+$, the distance between the $C_2H_5^+$ fragment and the H_2 subunit is 2.5 Å. The H–H length is 0.783 Å, while that of the free H_2 is 0.734 Å at the same level of the theory. The skeleton of the $C_2H_5^+$ fragment closely resembles an isolated classical $C_2H_5^+$ ion. The classical $C_2H_5^+$ is constructed with the methyl and methylene groups. The C–C bond length (1.425 Å) in the loose open $C_2H_7^+$ is close to that (1.415 Å) in the classical $C_2H_5^+$, and an intermediate between the single and double C–C bond lengths. C–H linkage on the methyl and methylene group in the loose open $C_2H_7^+$ have similar bond lengths and bisector angles to those in the classical $C_2H_5^+$. Apparently, the loose open form is a weakly bound complex of the classical open ethyl cation and the hydrogen molecule.

The transition state geometry and the transition vector connecting the loose and tight complexes are illustrated as C in Fig. 4.

At the SCF level, the energy gap between the tight and loose form is 2.2 kcal mol^{-1}. Inclusion of correlation effects increases the value to 11.8 kcal mol^{-1}. The electron correlation for the tight open form is greater

Table 5. Theoretical and Experimental Vibrational Frequencies for C_2H_6

[cm^{-1}]

ν_i	Symmetries	Calculated frequencies	Scaled frequencies[a]	Observed frequencies[b]
1	a_{1g}	3157	2841	2899(58)[c]
2	a_{1g}	1546	1391	1375(−16)
3	a_{1g}	1046	941	993(52)
4	a_{1u}	317	285	275(−10)
5	a_{2u}	3168	2851	2954(103)
6	a_{2u}	1534	1381	1379(−2)
7	e_u	3203	2883	2994(111)
8	e_u	1623	1461	1486(25)
9	e_u	885	797	820(24)
10	e_g	3232	2909	2963(54)
11	e_g	1624	1462	1460(−2)
12	e_g	1326	1193	1155(−38)

a) A universal scale factor employed is 0.9. b) Experimental values are for the staggered form of C_2H_6. c) Values in parentheses are differences between theory and experiment.

Table 6. Tentative Assignments of Fundamentals and Combination Band (a) for the Bridged $C_2H_7^+$ (C_2), (b) for Bridged $C_2H_7^+$ (C_{2v}). All calculated frequencies are multiplied by 0.9.

[cm^{-1}]

(a) ν_i	Symmetries	Calculated frequencies	Observed frequencies	(b) ν_i	Symmetries	Calculated frequencies	Observed frequencies
7+14+17		4135	3917(218)[b]	7+15+17		4100	3917(183)[b]
2×7		4070	3845(225)	2×7		4042	3845(197)
2+17		3952	3762(190)	2+17		3965	3762(203)
4+17		3912	3726(186)	4+17		3923	3726(197)
7+8		3800	3667(133)	7+8		3758	3667(91)
1	B	3062(0.52)[a]	3128(−66)	1	B_2	3075(0.64)[a]	3128(−53)
2	A	3061(0.33)		2	A_2	3063(0.00)	
3	A	3024(0.49)	3082(−58)	3	A_1	3027(0.77)	3082(−55)
4	B	3021(0.69)		4	B_1	3021(0.75)	
5	A	2903(0.01)		5	A_1	2904(0.04)	
6	B	2899(0.39)	2945(−46)	6	B_1	2901(0.45)	2945(−44)
7	B	2035(17.40)		7	B_1	2035(18.37)	
8	A	1765(0.34)		8	A_1	1765(0.34)	
9	B	1415(0.02)		9	A_1	1406(0.67)	
10	A	1409(0.01)		10	B_2	1395(1.05)	
11	B	1409(0.75)		11	A_2	1395(0.00)	
12	A	1396(0.70)		12	B_1	1395(0.00)	
13	A	1336(0.00)		13	A_1	1338(0.04)	
14	B	1209(1.69)		14	B_2	1206(0.04)	
15	B	1135(0.41)		15	B_1	1174(1.97)	
16	A	1063(0.00)		16	A_2	1039(0.00)	
17	B	891(9.75)		17	B_1	891(11.06)	
18	B	783(0.05)		18	A_1	767(0.06)	
19	A	318(0.08)		19	B_2	309(0.01)	
20	A	178(0.01)		20	A_1	301(0.12)	
21	A	165(0.04)		21	B_2	106i(0.01)	

a) Intensities in D^2 A^{-2} amu^{-1}. b) Differences between theory and experiment.

than that for the bridged C_2 and C_{2v} forms. The difference between the two bridged and the tight open form is reduced to 6.6 and 7.8 kcal mol^{-1} by ZPE. The experimental value of the dissociation energy into the most stable $C_2H_5^+$ and H_2 by Hiraoka et al. is 4.0 kcal mol^{-1}.[16] At the highest level of theory considered, SD(Q)CI+ZPE, the dissociation energy is 3.3 kcal mol^{-1}.

The electron correlation of the loose open $C_2H_7^+$ form is smallest. According to the previous work, the distance of C···H_2 in the open structure is reduced with the inclusion of polarization functions and electron correla-

Table 7. Tentative Assignments of Fundamentals and Combination Band (a) for the Tight Open $C_2H_7^+$ and (b) for the Loose Open $C_2H_7^+$. All calculated frequencies are multipiled by 0.9.

[cm^{-1}]

(a) ν_i	Symmetries	Calculated frequencies	Observed frequencies	(b) ν_i	Symmetries	Calculated frequencies	Observed frequencies
1+17		4065	3964(101)$^{b)}$	1	A'	4055 (1.52)$^{a)}$	3964(91)$^{b)}$
1+19		3750		6+10		3950	
1	A'	3091(2.19)$^{a)}$		6+11		3863	
2	A''	2972(0.02)		2	A''	3045(0.76)	
3	A'	2954(0.02)		3	A''	2988(0.16)	
4	A''	2942(0.90)	2825(117)	4	A'	2940(0.11)	
5	A'	2884(0.03)		5	A'	2910(0.20)	2825(85)
6	A'	2880(0.30)	2762(118)	8+9		2754	2762(−8)
7+16		2855		8+10		2658	2683(−25)
7+17		2750	2683(67)	6	A'	2638(2.46)	2601(37)
7+18		2627	2601(26)	9+10		2631	
7+19		2540	2521(19)	2×10		2622	
				10+11		2535	2521(14)
7	A''	1881(1.65)		7	A'	1493(0.11)	
8	A'	1468(0.13)		8	A'	1434(0.33)	
9	A'	1453(0.14)		9	A''	1320(0.44)	
10	A''	1443(0.36)		10	A'	1311(1.11)	
11	A'	1403(0.10)		11	A''	1224(0.51)	
12	A'	1325(0.46)		12	A''	1184(0.11)	
13	A''	1304(0.36)		13	A'	1074(0.74)	
14	A'	1148(0.02)		14	A''	804(0.05)	
15	A''	1129(0.07)		15	A''	485(0.21)	
16	A'	974(0.39)		16	A'	474(1.42)	
17	A'	869(0.63)		17	A''	423(0.23)	
18	A''	746(0.40)		18	A''	208(0.03)	
19	A'	659(1.06)		19	A'	179(0.53)	
20	A''	282(0.00)		20	A'	141(0.39)	
21	A''	191(0.06)		21	A''	61(0.13)	

a) Intensities in $D^2\ A^{-2}\ amu^{-1}$. b) Differences between theory and experiment.

tion. It seems reasonable that correlation effects make little contribution to the geometry of the loose open form because the interaction between the $C_2H_5^+$ groups and the H_2 moiety is expected to be much smaller in such a long distance. As discussed above, the C–H bonds on the $C_2H_5^+$ fragment in the loose open form are slightly changed from the classical $C_2H_5^+$. There is an alternative form to the loose complex. In this form, the H_2 subunit is rotated by 90° and the corresponding energy is close to that of the loose open form. The energetics of the loose open form and its alternative form indicates nearly free rotation of the H_2 subunit can occur in the loose complex. In the alternative form of the loose open $C_2H_7^+$, the geometric parameters remain almost constants. The loose open $C_2H_7^+$ is expected to have little reorganization of the electrons. Komormicki et al. also reached the similar conclusion on CH_5^+. In that case, the distance of $C\cdots H_2$ subunit is only 1.15 Å.[41)]

We displayed contour maps of the density difference, $\rho(C_2H_7^+)-\rho(C_2H_5^+)-\rho(H_2)$ for the loose and tight open $C_2H_7^+$ in Fig. 7. The full and broken lines denote the increase and decrease of electron density, respectively. The classical $C_2H_5^+$ is formed by CT from the π orbital of C_2H_4 to H^+. Then, the lobe of the antibonding π orbital in the position trans to the attached proton in $C_2H_5^+$ becomes very enlarged as compared to that of C_2H_4. This enhances the nature as an electron acceptor of $C_2H_5^+$. From the map of the loose complex, a hydrogen molecule attaches moderately to the antibonding π orbital of $C_2H_5^+$ with little reorganization of electron density in $C_2H_5^+$. The map of the tight complex shows that the three-center covalent bond is formed, which is due to the CT from the σ orbital of H_2 to $C_2H_5^+$. It also shows that a considerable redistribution of electron density has occurred. This corresponds to the change of hybridization from an sp^3 carbon to a penta-coordinated carbon.

Referring to Fig. 5, the stabilization energy of the loose complex relative to the classical $C_2H_5^+$ and a H_2 is only 1.9 kcal mol^{-1}. The activation barrier of the isomerization reaction for the tight complex is 3.7 kcal mol^{-1}.

Proton affinities are given in Table 4. The SD(Q)CI+ZPE results were shifted systematically. The theoretical gap between the bridged C_2 and C_{2v} form is only 1.2

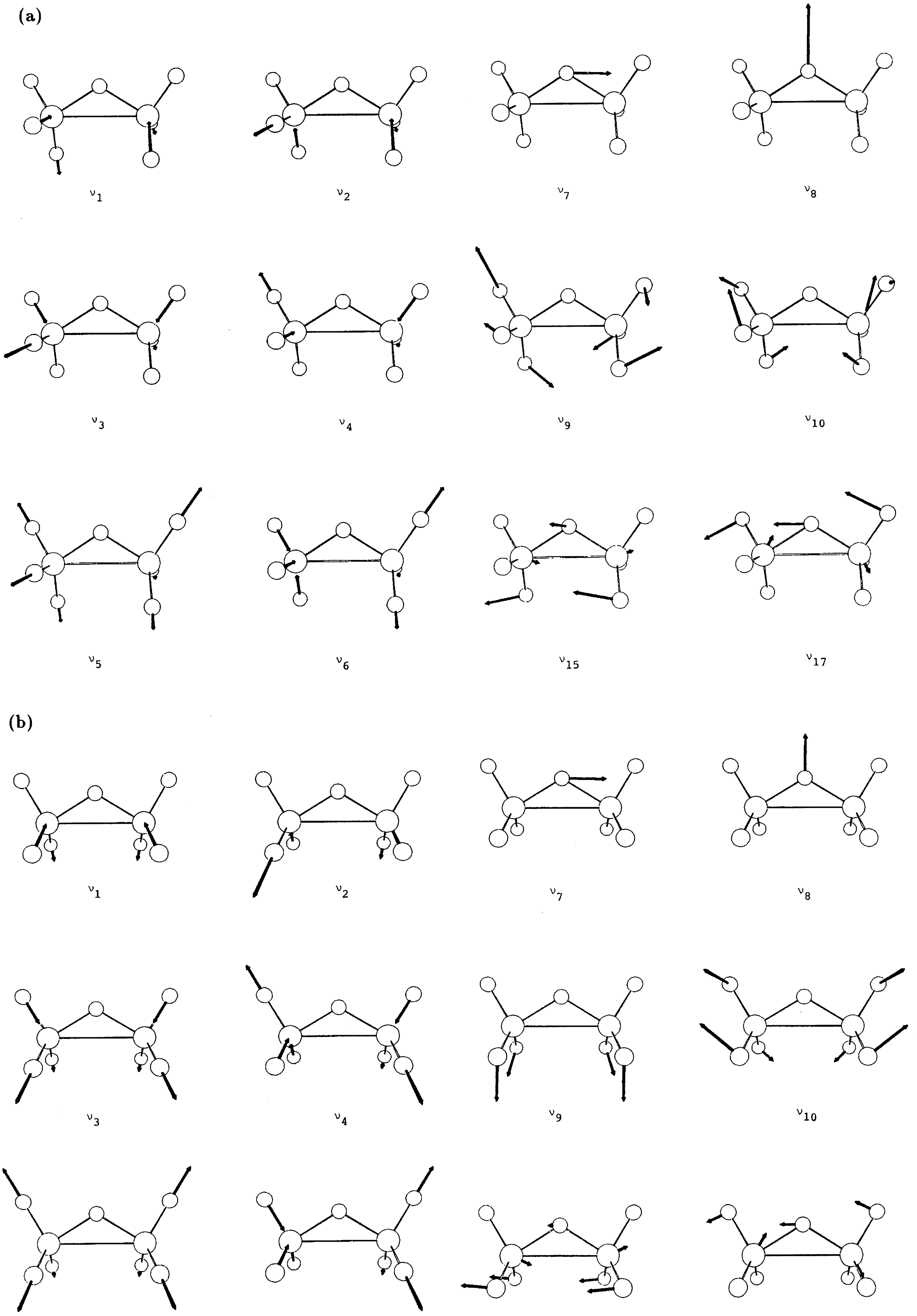


Fig. 8. (a) Normal modes of the bridged $C_2H_7^+$ (C_2), (b) Normal modes of the bridged $C_2H_7^+$ (C_{2v}).

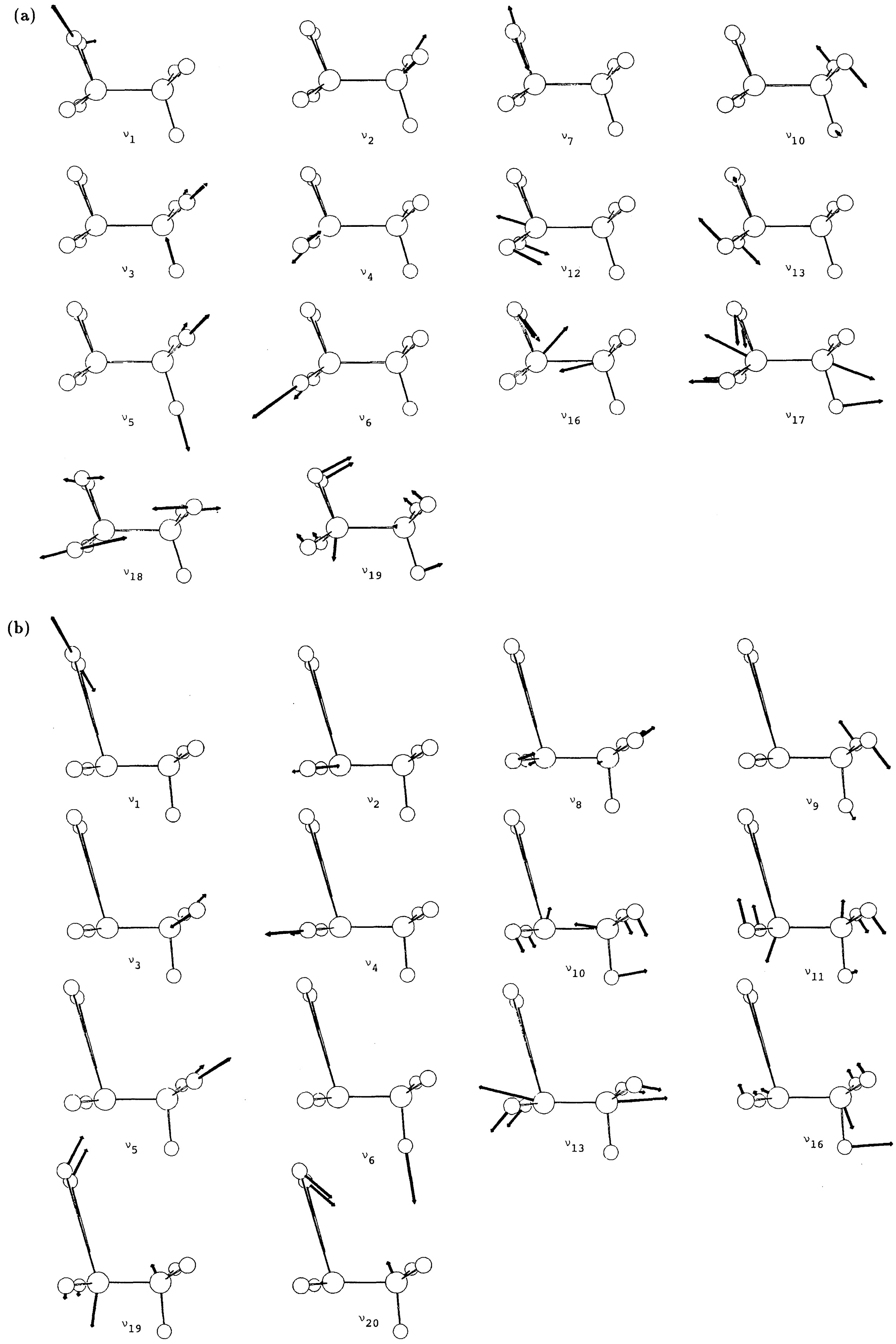


Fig. 9. (a) Normal modes of the tight open $C_2H_7^+$, (b) Normal modes of the loose open $C_2H_7^+$.

kcal mol^{-1}, so it is hard to separate the experimental values into each form. For the open form, the calculated gap between the tight and loose form is much larger (4.5 kcal mol^{-1}) and there exists an obvious difference in the two observed values. Agreement between the calculated gap of 4.5 kcal mol^{-1} and the experimental one of 4.6 kcal mol^{-1} is good.

2. Vibrational Analysis

Yeh, Price, and Lee have recorded IR spectra over 2000 cm^{-1} range and tried to assign the experimentally observed frequencies to the calculated ones.[22] In this work, we calculated the normal modes analysis with analytical second derivative techniques.

The agreement between theoretical and experimental vibrational frequencies is improved by scaling the raw theoretical results. In the present study, the value of 0.9 was used as the scaling factor. This factor is reported as a proper value at HF/6-31G* level for the molecules involving second row atoms by DeFrees et al.[40]

Table 5 presents a comparison of the theoretical and experimental frequencies for ethane. The scaled frequencies are close to the experimental ones. The worst case is the C–H asymmetric stretch and the difference is 111 cm^{-1}.

Table 6 lists calculated frequencies and the tentative assignments of theoretical predictions to experimental values for the bridged forms. From a comparison between the observed frequencies and intensities, the experimental peak of 2945 cm^{-1} can be assigned to the theoretical frequencies of 2899 cm^{-1} for the C_2 form and 2901 cm^{-1} for the C_{2v} form. The experimental peak of 3082 cm^{-1} can be assigned to two peaks for each form; either 3021 and 3024 cm^{-1} for the C_2 or 3021 and 3027 cm^{-1} for the C_{2v}. The peak of 3128 cm^{-1} can be assigned to the theoretical results of 3062 cm^{-1} for the C_2 and 3075 cm^{-1} for C_{2v}. The agreement of the theoretical predictions with the experimental frequencies is good. The worst difference between theory and experiment is only 66 cm^{-1}. This supports that the vibrational spectrum at 150 Torr arises form the bridged structure.

Some sets of the normal modes vectors for the bridged structures are shown in Fig. 8a and b. For the C_2 form, every motion substantially remains that of the parents species, the staggered C_2H_6. For the C_{2v} form, the parent species is the eclipsed C_2H_6.

The five features between 3600 and 3950 cm^{-1} are assigned to combination bands of the lower bands originated from the bridged structure by Yeh et al.[11] According to Table 6, the difference between theoretical and experimental frequencies is between 200 and 100 cm^{-1}. To consider the error of fundamentals, the agreement of combination bands is also good.

Tentative assignments for the tight and loose open structures is listed in Table 7. For the open form, comparison of fundamentals between theory and experiment is rather discouraging. The six experimental peaks at 2521, 2601, 2683, 2762, 2825, and 3964 cm^{-1} are thought to arise from the open structure. The vibrational frequencies of C–H stretch in ethane lie between 2895 and 2986 cm^{-1}. If the first five peaks are fundamentals, the red-shift is close to 400 cm^{-1}, while the computed lowest C–H stretch is 2880 cm^{-1} for the tight open form. For the loose open form, the lowest C–H stretch is 2638 cm^{-1}. However, the second lowest C–H stretch is 2910 cm^{-1}.

The feature at 3964 cm^{-1} disappears simultaneously with the five features below 2900 cm^{-1}. This suggests that they originate from the same form of $C_2H_7^+$. Therefore, the peak at 3964 cm^{-1} must come from the open structure. For the loose open form, theory predicts the peak of 4055 cm^{-1}. However, no fundamentals are computed above 3091 cm^{-1} for the tight open or bridged forms.

The six experimental peaks at 2521, 2601, 2683, 2762, 2825, and 3964 cm^{-1} can be explained in terms of combination bands. From Table 7, differences for the loose open form are generally smaller than ones for the tight open form. Referring to Tables 6 and 7, we see that fundamentals arising from the bridged and open forms are very close to each other. Even if fundamentals from the tight and loose open form exist in 3050—3150 cm^{-1} they must be masked by the peaks from the bridged forms which are energetically more stable.

The frequency of the H–H stretch in a free H_2 is 4161 cm^{-1} and that of H_2^+ is predicted about 2300 cm^{-1}. The experimental value of 3964 cm^{-1} is slightly lower than the frequency in H_2 and higher than that in H_2^+. This strongly supports that the 3964 cm^{-1} band can originates from the H–H bond stretching that is somewhat weakened on formation of the loose open complex. Some sets of the normal modes vectors for the loose and tight open structures are shown in Fig. 9a and b, respectively. For the loose open form, ν_1 corresponds to calculated 4055 cm^{-1} is a stretching of the attached H_2. In addition very sharp peak observed at 2601 cm^{-1} can be assigned by the frequency of 2638 cm^{-1} that is the stretching of C–H in the position trans to the attached H_2. The most reasonable conclusion may be that the additional bands balow 2900 cm^{-1} and feature at 3964 cm^{-1} in the spectrum observed at 60 Torr arise from the loose open form.

3. Conclusion

The present calculation predicts two isomers for both the bridged and open $C_2H_7^+$ ions. For the bridged structure, the C_2 and C_{2v} forms are calculated. The two structures have almost identical energies. For the open structure, a loose complex between a classical $C_2H_5^+$ ion and a H_2 molecule and a tight complex with three-center covalent bond are found. On the basis of the vibrational analysis of these four forms, the experimentally observed different behavior can be attributed to the changing ratio of the bridged C_2 structure to the loose open structure being probed spectroscopically. The final interpretation of the experimental data is that the spectrum at 150 Torr arises from the bridged C_2 form which is the most stable form of the protonated ethane. All peaks that have disappeared at 150 Torr come from the weakly bound complex that is dissociated upon absorbing a single IR photon.

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