J. Phys. Chem. A **1998,** *102,* 10903−10911

The Three Isomers of Protonated Ethane, $C_2H_7^+$

Allan L. L. East,*,† Z. F. Liu,‡ Claire McCague,† Karen Cheng,† and John S. Tse*,†

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada, and Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong, China

Received: September 8, 1998

The fluxional behavior of the protonated ethane ion was examined using both static and dynamic modeling. Static ab initio calculations, including perturbation theory (MP2), coupled cluster (CCSD(T)), and density functional theory, were used to locate various minima, saddle points, and G2-quality relative energies on the potential energy surface for atomic motions. In tandem, Car−Parrinello molecular dynamics simulations were performed to aid the stationary-point search and to examine the stabilities of various isomers at different temperatures. Predicted infrared spectra were also obtained from both techniques. Unlike most previous experimental and theoretical investigations which have focused upon the relative energies and stabilities of σ_{C-C}-protonated (bridged) structures and σ_{C-H}-protonated (open or "classical") structures, this work establishes the existence of a third isomer, the ion−molecule or solvated-ion complex $C_2H_5^+\cdots H_2$, which is the more likely candidate for the second isomer of experiments by Hiraoka and Kebarle and by Yeh, Price, and Lee. The open isomer may still be experimentally unknown. Peculiar discrepancies remain, however, and further experimental work is needed to resolve them.

Introduction

Protonated alkane molecules generally contain pentacoordinated carbon atoms and unusually extensive fluxional hydrogen-scrambling motions. For instance, protonated methane (CH_5^+) possesses a potential energy surface for fluxionality featuring 120 identical minima, each involving a 3-center−2-electron CH_2 moiety, with CH_2 internal rotation and H atom transfer paths which allow complete hydrogen scrambling with modest amounts of energy (the hindering barriers being only 0.1 and 0.8 kcal mol^{-1}, respectively).[1,2] CH_5^+ is not the best prototype for protonated alkanes, however, because (i) it lacks isomers possessing CCH 3-center−2-electron bonds which are also prevalent and (ii) it lacks dissociation channels for C−C bond fission. The protonated ethane ion, $C_2H_7^+$, is a better candidate in this regard. Unfortunately, for $C_2H_7^+$ there are currently disagreement and uncertainty concerning how many isomers there should be and which ones are being detected experimentally.[3,4] To address this problem, we have brought together our expertise in static and dynamic calculations on protonated methane[5−8] to raise the theoretical knowledge of $C_2H_7^+$ to the point where the internal dynamics can be properly summarized for the first time. Furthermore, our new results allow us to provide important new interpretations of published experimental results.

Pentacoordinated carbon atoms were possibly first postulated by Winstein and Trifan in 1952 to explain the rearrangement of the norbornyl cation in solution.[9] In that same year, gas-phase protonated methane was discovered by mass spectrometrists in the former USSR,[10] thus opening the door to a new class of overcoordinated compounds. A few years later, Meisels, Hamill, and Williams at the University of Notre Dame concluded that a fleetingly stable form of protonated ethane could account for some of their observations during experiments involving irradiation of atmospheric-pressure methane in a mass spectrometer.[11,12] They postulated that $C_2H_7^+$ existed in both an intermediate form (reaction 1) and a collisionally-stabilized form (reaction 2), formed from the reaction of CH_3^+ with CH_4.

$$CH_3^+ + CH_4 \rightarrow [C_2H_7^+] \rightarrow C_2H_5^+ + H_2 \qquad (1)$$

$$[C_2H_7^+] + M \rightarrow C_2H_7^+ + M \qquad (2)$$

$C_2H_7^+$ was first detected as an *m/z* peak of 31 in the high-pressure mass spectrum of ionized methane by Wexler and Jesse in 1962[13] and was subsequently detected by Munson, Franklin, and Field in a similar experiment,[14,15] with both groups supporting the postulates of the Notre Dame group of a high-energy form and a collisionally stabilized form.

Several studies of reaction 1 were performed from 1966 to 1973 using deuterium-labeled compounds, which indicated that substantial hydrogen scrambling occurs during the course of the exothermic reaction despite an apparently short-lived intermediate $[C_2H_7^+]$ complex.[16−20] After some early ab initio determinations of possible $C_2H_7^+$ conformations,[21,22] Olah and co-workers deduced that the σ bonds in alkanes could attract the extra proton to form 3-center CCH or CHH bonds.[23] The resulting structures (with either a CCH or CHH 3-center bond) have been called the nonclassical (or bridged) and classical (or open) forms, in crude accord with Winstein's earlier work, although neither of these pentacoordinated structures should be considered a classical one.[3] The bridged form contains two pentacoordinated carbons while the open form contains only one.

In 1975, Hiraoka and Kebarle investigated the possible isomers of $C_2H_7^+$ by producing $C_2H_5^+$ ions via reaction 1 and examining their ensuing reaction (reaction 3) with copious

---

† National Research Council of Canada.
‡ The Chinese University of Hong Kong.

10.1021/jp983640l CCC: \$15.00 © 1998 American Chemical Society
Published on Web 12/08/1998

amounts of H_2 carrier gas.[24] Observing reaction rates and

$$C_2H_5^+ + H_2 \rightleftharpoons C_2H_7^+ \qquad (3)$$

equilibrium constants which varied dramatically with temperature, they concluded that they were indeed observing two different isomers of $C_2H_7^+$, which they took to be the bridged and open forms, although the H_2 moiety of the open form appeared somewhat removed from the rest of the ion.

In 1989, Yeh, Price, and Lee examined some infrared bands of $C_2H_7^+$ using a two-color laser scheme, where the $C_2H_7^+$ ions were cooled in a supersonic expansion.[25] By observing various spectral differences upon variations in jet backing pressure, carrier gas ratio, and other affectations, they concluded that they were also observing two isomers of $C_2H_7^+$, which they also took to be the bridged and open forms.

While the Hiraoka and Kebarle conclusions have not been questioned, the Yeh−Price−Lee results did cause concern. In late 1993, Obata and Hirao employed ab initio RHF/TZ2P optimizations and harmonic frequency calculations for $C_2H_7^+$ and found minima for both a “tight” and a “loose” version of the traditional open structure, as well as two forms for the bridged structure.[3] They proposed that their loose open form represents the second Yeh−Price−Lee isomer, largely on the basis of somewhat speculative infrared combination band arguments. They also left confusion as to whether there were two, three, or four isomers of the $C_2H_7^+$ ion. In early 1994, a concurrent theoretical paper by Carneiro et al.[4] appeared but offered different conclusions. This work surveyed the potential energy surface using ab initio methods, finding 17 different stationary points (including six minima) at the MP2(full)/6-31G(d, p) level of theory, and also computed harmonic frequencies. The authors concluded that only the bridged forms and one of the (“tight”) open forms should exist and be observable but that the open form could not explain the second set of infrared peaks observed by Lee and co-workers.[25] They did find minima for loose open forms but discounted them as being too thermodynamically unstable.

In this paper, we present the new claim that there are in fact *three* basic isomers of $C_2H_7^+$: the bridged form, the (tight) open form, and the (loose) solvated-ion complex $C_2H_5^+\cdots H_2$. We employ traditional ab initio methods to extend the number of known potential surface stationary points from 17 to 27 and compute more accurate relative energies, and we employ ab initio molecular dynamics with the Car−Parrinello method to demonstrate dynamic stabilities. Both methods are used to produce rough predictions of the IR spectrum. The experimental observations are then rediscussed in light of these valuable new data.

Theoretical Methods

Geometry optimizations of various minima and saddle points were performed using analytic gradients calculated at two different levels of theory, namely second-order Møller-Plesset perturbation theory (MP2) and density functional theory (DFT). The DFT calculations employed the Becke 1988 gradient-corrected exchange and Lee−Yang−Parr gradient-corrected correlation energies (BLYP). These calculations all used the 6-31G(d,p) basis set, and no electrons were frozen in the correlation treatment. Harmonic frequencies at stationary points were calculated from analytic second derivatives and used to compute zero-point vibrational energies (ZPVE) as well as predict infrared spectra. These calculations were performed with the *Gaussian 94* code.[26]

Higher-level energetics were calculated using the coupled-cluster theory CCSD(T) with the cc-pVTZ basis set, using the MP2 geometries. Here the carbon 1s electrons were frozen in the correlation treatment. The size of the basis set (158 basis functions) makes this calculation exceed G2 theory[27] (at most 141 basis functions) in quality. These calculations were performed with the MOLPRO code.[28]

Ab initio (Car−Parrinello) molecular dynamics calculations were performed with the CPMD program suite[29] locally modified for fixing the center-of-mass motion in the dynamical calculations. Norm-nonconserving Vanderbilt ultrasoft pseudopotentials with an energy cutoff of 25 Ry[7,30] were used in the initial exploration of the potential energy surfaces of different isomers. The final results reported here were performed with the norm-conserving Troullier−Martin pseudopotentials[31,32] with an energy cutoff of 35 Ry. These were used in the computation of BLYP energies and forces. All calculations were performed with a simple cubic simulation box of size 20 au, a time step of 4 au, and a typical run length of 30 000 iterations (3 ps). To study the interconversion mechanism and thermal stability of the different isomers, trajectories with different initial conditions (conformation and temperature) were studied. The infrared vibrational spectra for the isolated isomers were calculated at very low temperature, typically 50−125 K, in order to avoid structural interconversions. The infrared spectra were calculated from the Fourier transform of the quantum polarization vectors computed from the Berry phase scheme.[33,34]

For infrared spectral predictions, our methods have complementary strengths. The CCSD(T) energies suggest that the MP2 potential surface is of high quality, and therefore the MP2 harmonic force field (HFF) frequencies are reliable, but they are difficult to apply to the $C_2H_7^+$ spectrum because of the neglect of potentially large H-scrambling anharmonicities and the inability to predict combination or overtone intensities. The CPMD-simulated infrared spectra will, in principle, include combination and overtone intensity, as well as anharmonicity, and hence offers a possible means of accounting for these spectral effects.

Results

Stationary Points. Carneiro et al.[4] reported 17 stationary-point conformations found on the MP2/6-31G(d,p) potential energy surface for $C_2H_7^+$. Building upon this excellent foundation, we reproduced these and added 10 more stationary points to this list, using the same level of theory, and the complete tabulations appear in Figures 1 and 2. As well, the corresponding points that existed on the DFT/6-31G(d,p) potential surface were also located. We introduce a labeling scheme for these conformations, not only for reference purposes but also for providing insight into the nature of the stationary points and providing a valuable means for describing and locating stationary points of higher protonated alkanes in the future. The crux of the labels is the envisaging of $C_2H_7^+$ to behave like CH_5^+ but with a methyl group substituted for one of the H atoms. This labeling scheme we now describe.

CH_5^+ has 120 symmetrically equivalent minima in which the CH_2 3-center bond plane is eclipsed to a remaining CH bond. Upon methyl substitution, these minima split into four unique groups, labeled B1, B2, O1, and O2. If the substituted position is in the 3-center bond, a bridged structure results (B1, B2), and if not, an open structure results (O1, O2). Also, the newly added methyl group can generally be positioned either eclipsed or staggered with respect to the original methyl group, for which we append an “e” or “s” to the conformer designation. Note the special case where B1s = B2s.

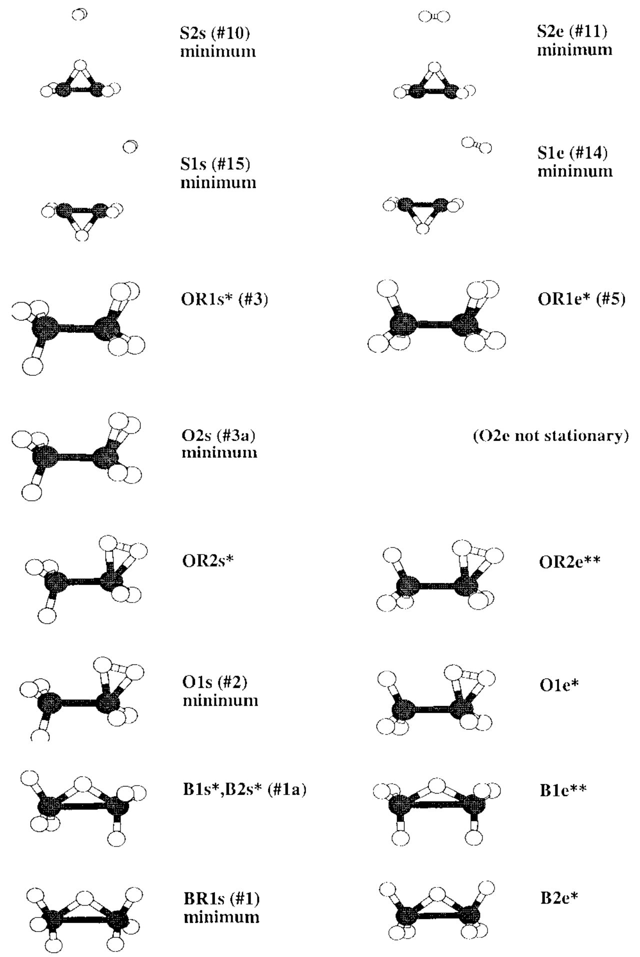

Figure 1. B, O, BR, OR, and S stationary-point geometries of $C_2H_7^+$, from MP2/6-31G(d,p) optimizations. The number of asterisks indicates the number of imaginary frequencies. The labels of ref 4 appear in parentheses.

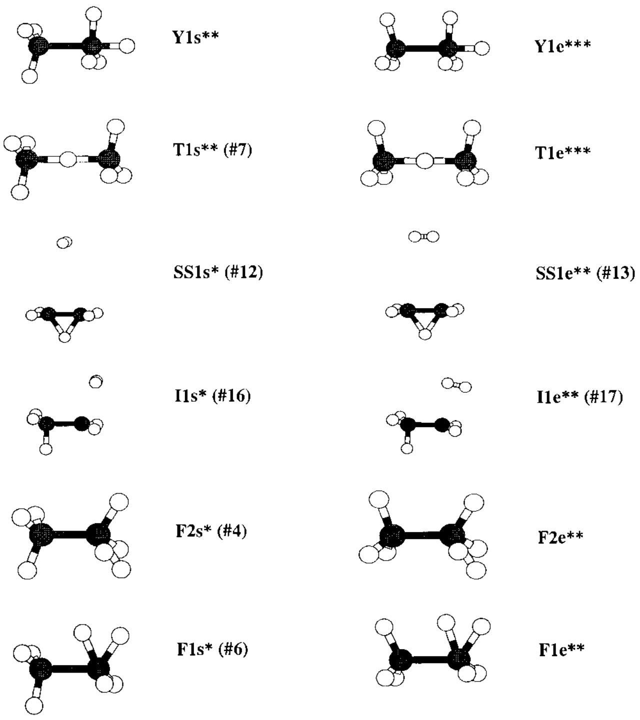

Figure 2. F, I, SS, T, and Y stationary-point geometries of $C_2H_7^+$, from MP2/6-31G(d, p) optimizations. The number of asterisks indicates the number of imaginary frequencies. The labels of ref 4 appear in parentheses.

CH_5^+ also has 120 symmetrically equivalent internal rotation transition states in which the CH_2 3-center bond plane is staggered with respect to the remaining CH bonds; upon substitution, these conformations split into three unique groups, labeled BR1, OR1, and OR2. BR1 designates the substitution at the 3-center bond, creating a bridged conformation, while OR1 and OR2 denote open conformations arising from substitution at a 2-center bond. CH_5^+ also has 60 symmetrically equivalent flip transition states, which upon substitution split into three unique groups, labeled F1, F2, and F3. These conformational transition states allow interconversion between B and O forms, O and O forms, and B and B forms, respectively. Our failed searches for F3e and F3s suggest however that these two forms do not exist as stationary points in $C_2H_7^+$.

CH_5^+ has some higher-energy saddle points of high symmetry which were found by Schleyer and Carneiro.[35] Their transition state for H2 "tumbling" we designate with a T, and Carneiro et al.[4] found a $C_2H_7^+$ analogue with methyl substituted for the furthest hydrogen (Tls), which was surprisingly low in energy. We investigated a $C_2H_7^+$ form (Y1) based on their CH_5^+ trigonal bipyramid with the Y-shaped equatorial hydrogen atoms, but this was found to be rather high in energy. Also in $C_2H_7^+$ are the solvated-ion $C_2H_5^+\cdots H_2$ minima and corresponding transition states, found by Carneiro et al.[4] and Obata and Hirao,[3] which we label S (for solvated-ion minima), I (for "in−out" transition states between S and O forms), and SS (for transition states between S forms). We also label dissociation asymptotes A1 (for $C_2H_5^+ + H_2$), A2 (for $CH_3^+ + CH_4$), and A3 (for $C_2H_6 + H^+$).

Table 1 lists the relative energies of these conformations, with the right-hand column providing the best estimates. The ZPVE corrections are taken as half the sum of all positive harmonic frequencies for that conformation, as is traditional but not always appropriate. The DFT potential surface has the essential features but is a more simplified surface, missing roughly one-third of the stationary points found with MP2, and its agreement with CCSD(T) energetics is not as quantitative. We tested the cc-pVTZ basis set for basis set superposition error with the counterpoise correction and found it to be less than 0.1 kcal mol^{-1} for $C_2H_5^+\cdots H_2$ (S2s), in accord with similar results for $CH_5^+\cdots H_2$.[36] Figure 3 is a summary of our best results and should give the reader a quick guide to the relative energies of these various conformations.

From careful inspection of these stationary points, one has a much better understanding of the internal dynamics of $C_2H_7^+$ than was known before. We can now predict that, at cold temperatures, the ion possesses three isomeric forms. The lowest-energy form is the bridged isomer, which features a 3-center−2-electron CCH bond and possesses two labile internal rotation modes, namely the methyl−methyl torsion and the revolution of the bridging hydrogen about the CC bond. The open isomer features a 3-center−2-electron CHH bond and possesses two different internal rotation modes, these being the methyl rotation and the spinning of the CHH 3-center−2-electron bond. The solvated-ion isomer features an H_2 group roughly 3 Å from the CC bond and possesses two particularly uninhibited internal rotation modes, namely the propeller-like spinning of the H_2 group and the log-rolling motion of the $C_2H_5^+$ unit about its CC bond.

To address the question of stability of the solvated-ion isomer, we looked at a set of three H_2-solvated cations (inspired by a

TABLE 1: Relative Energies (kcal mol^{-1}) for Conformations of $C_2H_7^+$

conformn[a]	MP2 6-31G(*d*, *p*)	DFT 6-31G(*d*, *p*)	CCSD(T)[b] cc-pVTZ	ZPVE[c]	MP2 +ZPVE	CCSD(T) +ZPVE
BR1s	0.00	0.00	0.00	0.00	0.00	0.00
B1s*	0.30	0.10	0.21	−0.27	0.03	−0.06
B2e*	0.89	0.67	0.80	−0.18	0.70	0.62
B1e**	3.29	1.48	2.65	−0.98	2.30	1.67
OR1s*	5.32	8.01	5.37	−1.69	3.64	3.69
T1s**	6.24	2.60	6.28	−2.56	3.68	3.72
T1e***	6.55	2.83	6.51	−2.75	3.81	3.76
O2s	5.32	*d*	5.40	−1.52	3.80	3.89
F2s*	6.50	9.08	7.21	−2.15	4.36	5.07
OR2s*	6.16	8.94	6.36	−1.16	5.00	5.19
OR1e*	7.34	9.72	7.30	−1.82	5.52	5.48
O1s	6.07	8.77	6.38	−0.87	5.21	5.51
F2e**	8.26	*d*	8.71	−2.55	5.72	6.16
F1s*	7.20	8.87	7.94	−1.48	5.72	6.46
OR2e**	9.26	*d*	9.15	−1.50	7.76	7.64
F1e**	9.22	*d*	9.66	−1.82	7.40	7.84
O1e*	9.13	*d*	9.21	−1.34	7.80	7.88
S2s	15.06	16.17	15.95	−7.12	7.94	8.83
S2e	15.05	16.23	15.99	−7.09	7.96	8.90
S1s	15.50	*d*	16.51	−7.43	8.07	9.08
S1e	15.48	*d*	16.52	−7.39	8.09	9.13
SS1e**	15.65	17.46	16.86	−7.73	7.92	9.13
SS1s*	15.61	17.40	16.78	−7.63	7.98	9.15
I1s*	19.94	*d*	18.52	−6.06	13.89	12.47
I1e**	20.09	*d*	18.64	−6.08	14.01	12.56
Y1s**	17.06	12.92	16.76	−2.63	14.43	14.13
Y1e***	20.86	15.78	19.95	−3.12	17.74	16.83
A1	16.00	17.62	17.56	−7.98	8.01	9.58
A2	39.71	44.79	40.98	−4.49	35.23	36.49
A3	144.72	151.86	146.41	−5.57	139.15	140.84

[a] Conformations in bold are the minima on the MP2 potential energy surface. [b] CCSD(T) energies were computed at MP2/6-31G(d,p) geometries. [c] Zero-point vibrational energies (ZPVE) were computed as half the sum of all positive MP2/6-31G(d,p) harmonic frequencies. [d] These stationary points do not exist on the DFT potential energy surface.

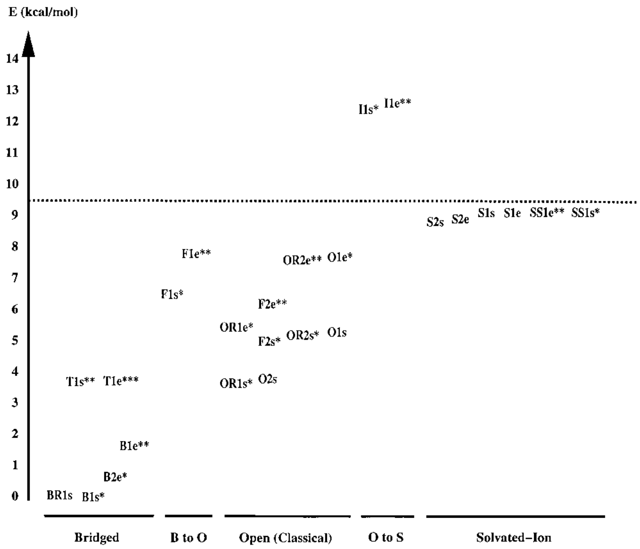

Figure 3. Schematic diagram depicting relative energies of the minima and saddle points of $C_2H_7^+$. Energies are CCSD(T) ones with ZPVE corrections (see Table 1).

TABLE 2: Dissociation Energies (kcal mol^{-1}) for $A^+\cdots H_2 \rightarrow A^+ + H_2$

ion complex[a]	r_e[b]	D_e[c]	D_0[c,d]
$H_3^+\cdots H_2$	1.33	8.3	5.4
$CH_5^+\cdots H_2$	1.97	3.3	1.5
$C_2H_5^+\cdots H_2$	2.30	1.6	0.75

[a] Geometries were optimized using MP2(full)/6-31G(d,p). All three complexes featured the H_2 group closest to an H atom of the 3-center−2-electron bond. [b] Distance (in Å) from the H_2 midpoint to the nearest H atom of the core ion, using the MP2/6-31G(d,p) geometry. [c] Energy computed via CCSD(T)/cc-pVTZ using MP2(full)/6-31G(d,p) geometries. The inferior MP2(full)/6-31G(d,p) values for D_e (5.0 for $H_3^+\cdots H_2$, 2.1 for $CH_5^+\cdots H_2$, and 0.9 for $C_2H_5^+\cdots H_2$) are roughly 40% smaller. [d] Includes ZPVE corrections, computed as half the sum of all positive MP2/6-31G(d,p) harmonic frequencies.

brief discussion by Kim et al.[36]). We calculated the energies for the binding of H_2 to H_3^+ and CH_5^+ as well as to $C_2H_5^+$, using MP2 geometries and CCSD(T) single-point energies as in Table 1; the results are displayed in Table 2. The $C_2H_5^+\cdots H_2$ isomer of $C_2H_7^+$ is roughly half as bound as the experimentally known[37−39] $CH_5^+\cdots H_2$. The bond strengths correlate very well with the distance of the H_2 group to the nearest H^+ atom of the 3-center−2-electron bond. For a more accurate estimate of the binding energy, we applied a basis set correction (from cc-pVTZ to aug-cc-pVTZ using MP2 binding energies) and the conversion from D_0 to ΔH^{130K} for $C_2H_5^+\cdots H_2$, which boosts the binding energy to 0.75 + 0.32 + 0.40 = 1.5 kcal mol^{-1} at 130 K. The uncertainty is probably 0.5 kcal mol^{-1}, in view of the approximations involved. Considering the temperature ranges at which the equilibria were observed for $H_3^+\cdots H_2$ (230−330 K)[40,41] and $CH_5^+\cdots H_2$ (65−105 K),[37] one might expect to see $C_2H_5^+\cdots H_2$ only below 100 K.

The three isomers of $C_2H_7^+$ are separated by classical barriers which potentially might not be traversable at cold temperatures. Figure 4 is a schematic potential surface for a hypothetical dissociation path (to the lowest asymptote, $H_2 + C_2H_5^+$) in which $C_2H_7^+$ passes from its bridged global minimum through the open and solvated-ion conformations before dissociating. Figure 4 includes not only our best results but also our best alignment of the equivalent curve of Hiraoka and Kebarle (their Figure 9)[24] for later discussion.

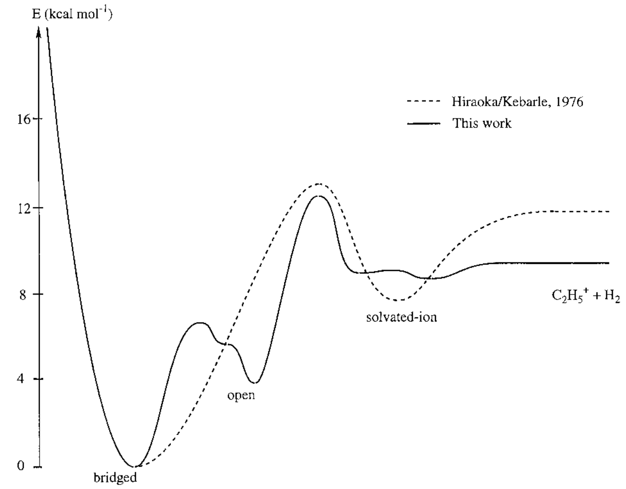

Figure 4. Rough schematic of a minimum-energy dissociation pathway from the lowest-energy bridged form of $C_2H_7^+$. The solid line arises from our CCSD(T)+ZPVE energies. The dashed line is the experimentally-deduced curve of ref 24; note that this curve contains temperature effects which are as large as 2 kcal mol^{-1} (see text).

Vibrational frequencies from harmonic force fields (HFF) were obtained at all MP2 and DFT stationary points. For presentation, we have chosen merely to generate simple infrared spectra (Figure 5) from the MP2 and DFT results at three minima (BR1s for bridged, O2s for open, and S2s for solvated-ion) which will aid in the discussion of infrared absorptions. To mimic true anharmonic fundamentals, these spectra employed harmonic frequencies which for BLYP-DFT were unscaled and for MP2 were scaled by 0.94,[42] with calculated IR intensities from the double-harmonic approximation[43] and an arbitrary Gaussian-peak width of 5 cm^{-1}. In Figure 5, the similarity of the MP2 and BLYP-DFT HFF spectra are quite apparent, demonstrating that we can have some faith in the DFT potential surface for the molecular dynamics simulations. These six HFF spectra in Figure 5 possess neither combination nor overtone bands, nor any particular anharmonic shifts due to fluxional behavior.

Molecular Dynamics Simulations. Due to the tunneling abilities of hydrogen atoms, we cannot expect our classical molecular dynamics (MD) simulations to produce high-accuracy results for the $C_2H_7^+$ hydrogen-scrambling system.[44] Nevertheless, there are two semiquantitative problems that cannot easily be addressed from static calculations but problems for which such dynamical simulations could be well suited: (i) Can we test for possible kinetic (thermal) stability of these various isomers, and (ii) can we produce IR spectra from the simulations of sufficient quality to get an idea of anharmonic hydrogen-scrambling effects and the presence of combination/overtone band intensities?

Hence, we performed simulations at $T = 40-50$ K for all three isomers, plus a hotter (up to 800 K) simulation beginning with a bridged-isomer structure. We found that, given the approximations that were made, all three isomers behaved at 50 K as we had anticipated, holding their general isomeric structure for the 3 ps simulation time length. At 300 and 500 K, simulations starting from the open form always isomerized to the bridged form in less than 100 time steps (0.01 ps) during the temperature scaling. Only at 800 K was a mixture of bridged and open forms observed.

The CPMD infrared spectra suffered somewhat from relative intensity problems, which we attribute to insufficient sampling of the 21 vibrational degrees of freedom of this system. Converged relative intensities for the CPMD infrared spectrum of $C_2H_7^+$ appear to require a tremendous amount of computer time. It is also evident that even qualitative modeling of the experimental spectrum (top of Figure 5) will remain a challenge for the future. The simulated spectra that we show in Figure 5 come from the 50 K simulations (40 K for the bridged isomer) which we felt did the best job of sampling in their respective neighborhoods, on the basis of animations of the nuclear motions during the runs. In Figure 5, note the relatively overly intense peaks at 4060 cm^{-1} for the solvated-ion isomer (bottom spectrum in the figure) and at 2940 cm^{-1} for the open isomer (fourth from the bottom), which are indicative of limited sampling. On the more satisfying side, note the presence of intensity between 2600 and 2800 cm^{-1} and between 3300 and 3600 cm^{-1} in the spectra of the bridged and solvated-ion isomers, due to combination/overtone band(s) which cannot be predicted with the harmonic approximation. Also note the general red-shifting by 50−100 cm^{-1} of the C−H stretching fundamentals between 2900 and 3200 cm^{-1}, upon going from the HFF to the CPMD spectra, due to increased anharmonicity.

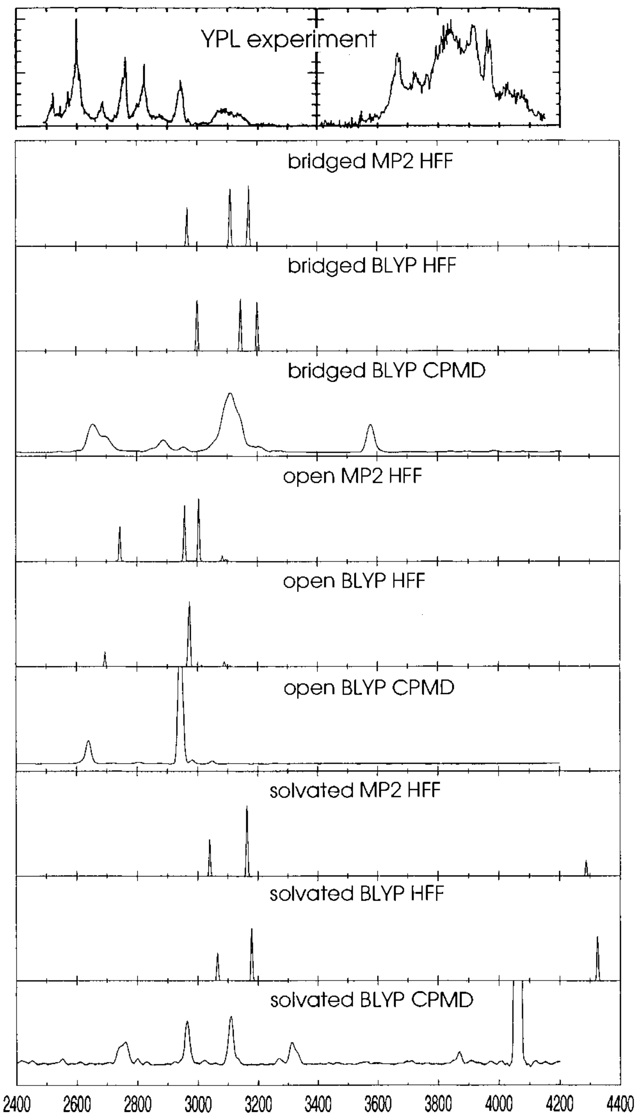

Figure 5. Predicted infrared spectra of $C_2H_7^+$. The top spectrum is from experiment.[25] HFF = harmonic force field predictions, using either scaled MP2 or unscaled BLYP calculations. CPMD = Car−Parrinello molecular dynamics predictions.

Discussion

The Hiraoka−Kebarle Experiments. Hiraoka and Kebarle[24] used a pulsed electron beam high-pressure ion source mass spectrometer to investigate $C_2H_7^+$. The ion was produced by electron impact upon a stream of H_2 gas containing small quantities of CH_4. Initially a series of very fast reactions culminates in reaction 1 (see Introduction), producing $C_2H_5^+$ ions which then lead to $C_2H_7^+$ by slower (millisecond) reaction with the H_2 bath gas in reaction (3).

Between −100 and +40 °C they observed one form of $C_2H_7^+$ labeled (b), and forward (association) rate constants for reaction 3 were determined from measurements of changing concentrations of $C_2H_5^+$ and $C_2H_7^+$ with time. The results suggested an exothermic association reaction but with a barrier, which helps trap the adduct without the assistance of third-body collisions, thus leaving a second-order rate dependence. Between 85 and 200 °C, the reverse of reaction 3 became fast enough that equilibrium constants could be measured. From a van't Hoff plot, the reaction enthalpy for the association reaction 3 was determined to be -11.8 ± 0.4 kcal mol^{-1}.

Between −160 and −130 °C, $C_2H_7^+$ was observed again, but in a different process in which equilibrium was established faster than in the hot experiments. These cold equilibria were more difficult to measure because of the competing formation of protonated propane. The form of $C_2H_7^+$ produced here was evidently different and was labeled a. The results suggested an exothermic association but *without barrier*, and the van't Hoff plot of the equilibrium data here produced a forward reaction enthalpy for reaction 3 of -4.0 ± 0.5 kcal mol^{-1}.

Hiraoka and Kebarle concluded that the strongly-bonded (b) form corresponded to the σ_{C-C}-protonated (bridged) form of $C_2H_7^+$ while the weakly-bound (a) form corresponded to a σ_{C-H}-protonated form. They considered the possibility that (a) was a loose $C_2H_5^+\cdots H_2$ complex and (b) was a tight $C_2H_5^+\cdots H_2$ complex (i.e., a true open or "classical" form) but discounted this assignment because they felt that (i) a barrier between loose and tight versions of $C_2H_5^+\cdots H_2$ was improbable and (ii) the bridged form should have appeared as a distinct form in their experiments.

All previous theoretical studies which we have found have not questioned the original assignment. We also agree that the lower-energy (b) form is the bridged isomer, because we have computed temperature and basis set corrections to convert our D_0 to ΔH^{373K} and obtained 12.0 kcal mol^{-1}, in accord with the 11.8 kcal mol^{-1} from experiment. However, the weakly-bound (a) form should be the ("loose") solvated-ion complex $C_2H_5^+\cdots H_2$, and not the open isomer, because $C_2H_5^+\cdots H_2$ is the only isomer which can dissociate without an activation barrier. Unfortunately, the experimental H_2 binding energy of the (a) form ($\Delta H^{130K} = 4.0 \pm 0.5$ kcal mol^{-1}) agrees with neither our value for the solvated-ion isomer ($\Delta H^{130K} = 1.5$ kcal mol^{-1}) nor our value for the open isomer ($\Delta H^{130K} = 7.0$ kcal mol^{-1}). Earlier, Carneiro et al.[4] had also demonstrated difficulties in reconciling this 4.0 kcal mol^{-1} experimental value with their value for the open isomer. We tested the MP2 geometry of the S2s solvated-ion isomer by varying the distance from H_2 to the bridging proton while computing MP2 and CCSD(T) energies with the cc-pVTZ basis set; the MP2 and CCSD(T) energy curves were in close agreement, demonstrating negligible energetic error from our use of MP2 geometries.

One might build a case for experimental overestimation. The study of $H_3^+\cdots H_2$ by the same authors using the same apparatus[40] produced a bonding enthalpy which now appears to be 3 kcal mol^{-1} too high.[45] Note also that the authors do comment several times that the H_2 group appears significantly removed from the rest of the ion.[24] Unfortunately, the temperature range for this isomer (−130 to −160 °C, or 110 to 140 K) is *hotter* than the range at which $CH_5^+\cdots H_2$ was observed, suggesting a binding energy greater than that of $CH_5^+\cdots H_2$. This is not compatible with theoretical results and is most peculiar.

Our Car−Parrinello molecular dynamics runs also support the existence of a solvated- ion isomer. We performed a cold-temperature (50 K) molecular dynamics simulation in which the H_2 moiety was initially placed 3 Å away from the $C_2H_5^+$ ion, and despite the overly small DFT barrier for conversion to the more stable $C_2H_7^+$ forms, the H_2 group remained 3 Å away for the duration of the run. For the open form, we succeeded in its isolation only when we began the simulation in such a form and operated down at 50 K. It may be difficult experimentally to produce this "hanging-well" isomer.

Our conclusions challenge popular beliefs[3,4,25] concerning the Hiraoka−Kebarle $C_2H_7^+$ study. A new experimental determination of the binding energy of this isomer is highly desired to confirm our description.

The Yeh−Price−Lee Experiments. Yeh, Price, and Lee[25] used a mass spectrometer connected with a radio-frequency octopole ion trap to investigate $C_2H_7^+$. These ions were produced by electrode discharge in a stream of H_2 gas carrying small quantities of ethane. The effluent was vibrationally cooled through multiple collisions before being forced through a 75-μm nozzle and then rotationally cooled by the ensuing supersonic expansion. Ions of mass 31 ($C_2H_7^+$) were selected via a sector magnet and passed into the octopole ion trap, where they were interrogated by a two-color laser scheme. A tunable IR laser, operating between 2400 and 4200 cm^{-1}, excited the ions vibrationally, and a CO_2 laser provided further energy to the vibrationally excited $C_2H_7^+$ in order to overcome the dissociation barrier and break into H_2 and $C_2H_5^+$. The $C_2H_5^+$ ions were then mass-selected, and the $C_2H_5^+$ ion count was used as a measurement of the absorbance and was plotted as a function of the wavenumber of the first tunable IR laser.

They found two groups of peaks in the experiment. The first group were sharper peaks between 2400 and 2900 cm^{-1} with an additional one centered at 3964 cm^{-1}. Their common feature was their gradual disappearance with increased backing pressure and increased C_2H_6:H_2 ratio. Since increased backing pressure improves collisional cooling, the affected peaks should be due to a higher-energy isomer. Such an assignment was further supported by the fact that when the second laser was blocked, the peaks between 2400 and 2900 cm^{-1} were still observed, while at least 3200 cm^{-1} is required to dissociate the bridged form (the most stable form of $C_2H_7^+$). The other groups of peaks, from 2900 to 3200 cm^{-1} and from 3600 to 4200 cm^{-1}, were generally broader and independent of backing pressure.

The experimentalists, with the assistance of exploratory ab initio calculations, concluded that the spectrum was due to contributions from two isomers: the second group from the more stable bridged isomer and the first group from the higher-energy "classical" (open) isomer. However, the peculiar locations of the peaks have defied explanation to this day. The original ab initio calculations predicted the C−H vibrational frequencies for the open isomer to be between 2900 and 3100 cm^{-1}, while the experimental result apparently showed a 400 cm^{-1} red shift to 2520−2825 cm^{-1}. The 3964 cm^{-1} peak was hundreds of reciprocal centimeters higher than any predicted fundamental peak for the open isomer and close to the value for free H_2. Furthermore, Yeh et al. could only give speculative assignments to the mysterious absorptions between 3600 and 4200 cm^{-1} (attributed to combination and overtone bands of the bridged isomer) which relied heavily on the low-level ab initio predictions and could not account for peculiar broadening of particular peaks in this range.

We now argue that the first group of peaks, namely the bands between 2400 and 2900 cm^{-1} and the one centered at 3964 cm^{-1} in the Yeh−Price−Lee experiment, are due to the solvated-ion isomer rather than the open isomer. The temperature of this experiment (rotational temperature $<$40 K)[25] is likely cold enough for this isomer to form. Carneiro et al.[4] and Okabe and Hirao[3] had already concluded that open isomer forms could not account for these peaks, on the basis of further ab initio frequency calculations, but had conflicting opinions concerning the solvated-ion possibility. Armed with improved theoretical data, we now proceed to discuss the observed spectral features.

With regard to the relative widths of peaks, note that fluxional molecules and ions can display broad infrared transitions due to the dependence of certain fast vibrations upon slower ones. Classically, if the low-energy form of $C_2H_7^+$ were oscillating between the bridged and open conformations, a particular C−H stretching fundamental would not appear at the location predicted using the bridged structure or that of the open structure, but at some broadened average. Quantum mechanically, the broadening is due to hot-band versions of the C−H fundamental, excited from various low-lying fluxional (torsional or bending) states. The pressure-dependent peaks are generally sharper than the others, which we think might support of the assignment of the solvated-ion isomer to all of these peaks. The solvated-ion isomer consists of two rigid entities, with relative internal rotation motions which might have little effect upon the vibrations of either entity. The bridged form is less rigid due to its two internal rotation modes and, with increased energy, possible conversion to open and predissociated forms; hence this could be the reason for the increased broadening of its IR transitions. Such broadening was observed in desolvating CH_5^+.[39] This broadening would be mode-dependent. The particularly broad 3700−4000 cm^{-1} peak might be a feature of a dissociation having a barrier in the exit channel, since Figure 4 suggests that this barrier is in effect from 10 to 12 kcal mol^{-1}, or from 3500 to 4200 cm^{-1}.

With regard to combination/overtone bands, such intensity was observed in the CPMD spectra of only the bridged (2700, 2900, and 3600 cm^{-1}) and solvated-ion (2750, 3300, and 3870 cm^{-1}) isomers. These isomers both possess a bridging proton, and bridging-proton vibrations cause large ionic charge redistributions which provide tremendous IR intensity for the fundamentals (as observed in our spectra at lower wavenumbers). These motions, which can be labeled as parallel to or dissociating from the CC bond, were originally thought by Yeh et al. to be the most likely to generate overtone and combination bands of the bridged isomer. Such a band has been observed at 4230 cm^{-1} for the $H_3^+\cdots H_2$ complex.[45] For $C_2H_7^+$ the scaled MP2 frequencies for these parallel and dissociative motions, respectively, are 2065 and 1999 cm^{-1} for the bridged isomer and 721 and 2127 cm^{-1} for the solvated-ion isomer. Crude predictions for the one combination and two overtone bands which arise from these two modes *alone* would be 4000 cm^{-1} for the bridged isomer and 1400, 2800, and 4200 cm^{-1} for the solvated-ion isomer and hence offer possible explanations for not only the experimental absorptions just below 4000 cm^{-1} but also the ones near 2800 cm^{-1}.

The pressure-dependent band at 3964 cm^{-1} cannot be due to the open isomer because none of our open-isomer spectra predict any absorption intensity above 3200 cm^{-1}. Yeh et al. observed 0.9−1.1 cm^{-1} spacings in the P and R branches of this peak (see their Figure 7), which they argued could be produced by the open isomer, using a simple model of an a-type (parallel) band and the rotational constants of the open isomer (2.265, 0.617, and 0.607 cm^{-1} for the MP2 O2s structure). However, this spacing can also be similarly produced from the rotational constants of the bridged isomer (2.434, 0.474, 0.472 cm^{-1} for BR1s) and the near-oblate solvated-ion isomer (0.788, 0.639, 0.419 cm^{-1} for S2s). Figure 6 displays the simulated spectrum which would arise for the vibrational excitation of a *rigid* molecule having the solvated-ion S2s geometry, using identical rotational constants for the upper and lower vibrational states and a transition moment ratio of μ_a:μ_b = 1:2. This was our best simulation using *rigid* models for the S2s, O2s, and BR1s minima; however, since a rigid model is a very poor description of any isomer of $C_2H_7^+$, our figure is shown only to demonstrate that the open isomer is not the only isomer capable of producing the observed P and R branches. We also modeled the rotation−contortion energy levels of the open and solvated-ion isomers as generated by a general Hamiltonian,[5] testing various free internal rotation paths for both isomers. The pure rotation transitions are changed rather little, with all internal rotation transition spacings being significantly larger than 1 cm^{-1}.

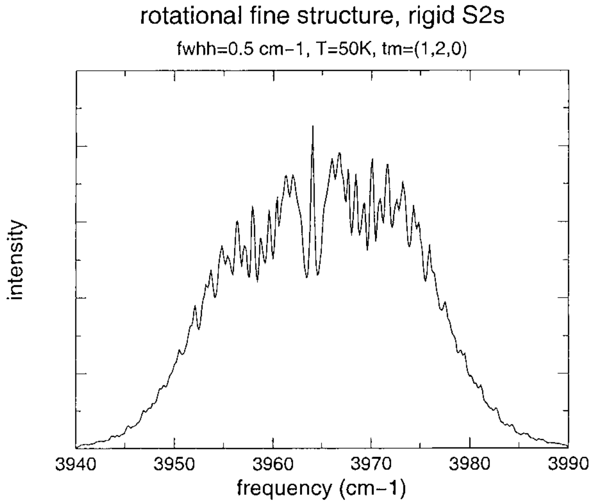

Figure 6. Resulting rotational fine structure for the 3964 cm^{-1} peak, assuming a rigid solvated-ion $C_2H_5^+\cdots H_2$ isomer, identical rotational constants for upper and lower states, Lorentzian peak full-width-at-half-height of 0.5 cm^{-1}, a 50 K Boltzmann distribution, and a transition moment of (μ_a, μ_b, μ_c) = (1, 2, 0).

This 3964 cm^{-1} band also *cannot* be due to the H−H stretch fundamental of the solvated-ion isomer, as assigned by Obata and Hirao.[3] This is ruled out by the correlation between H_2 bonding energy and the H−H stretch frequency. Figure 7 displays this correlation for three H_2-solvated systems and free H_2. Yeh et al. had argued that the 3964 cm^{-1} band was an H−H stretch fundamental, because it corresponds beautifully to a bonding energy of 4 kcal mol^{-1} as had been observed by Hiraoka and Kebarle.[24] This appears to be an unfortunate coincidence, since we see no evidence whatsoever for an isomer with these properties. We used Figure 7 to generate predictions (4116 cm^{-1} and 1.1 kcal mol^{-1}) for the true H−H stretch fundamental and bonding enthalpy of $C_2H_5^+\cdots H_2$, based on the average of two interpolated estimates from the relation

$$\frac{T(C_2H_5^+\cdot H_2) - T(H_2)}{T(A\cdot H_2) - T(H_2)} = \frac{E(C_2H_5^+\cdot H_2) - E(H_2)}{E(A\cdot H_2) - E(H_2)} \tag{4}$$

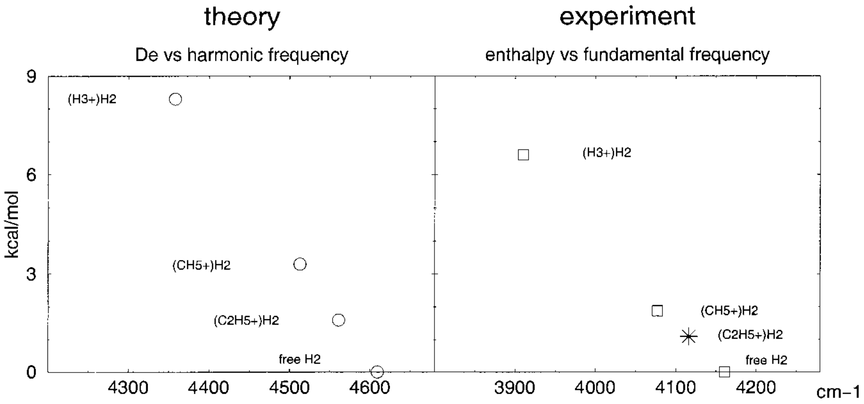

Figure 7. Correlation between H_2 vibrational frequency and dissociation energy of various H_2-solvated ions. Left-hand plot: D_e values from CCSD(T)/cc-pVTZ//MP2/6-31G(d, p), unscaled frequencies from MP2/6-31G(d, p). Right-hand plot: ΔH values for dissociation of H_2 from ref 41 ($H_3^+\cdots H_2$) and ref 37 ($CH_5^+\cdots H_2$), frequencies from ref 45 ($H_3^+\cdots H_2$) and ref 39 ($CH_5^+\cdots H_2$). The star indicates our prediction for $C_2H_5^+\cdots H_2$, based on the left-hand plot.

where T and E represent theoretical and experimental values of either the energy or vibrational frequency from Figure 7 and A is either H_3^+ or CH_5^+. The enthalpy prediction is in good agreement with our 1.5 ± 0.5 kcal mol^{-1} estimate earlier.

We feel that 3964 cm^{-1} must be an overtone of the solvated-ion isomer and that the 4 kcal mol^{-1} binding energy is somehow not as accurate as originally believed. This assignment is further supported by our Car–Parrinello simulations of the solvated-ion isomer, which display not only an H–H fundamental at 4060 cm^{-1} but also absorption at 3870 cm^{-1}. Our best guess for its assignment is the first overtone of the dissociative motion of the bridging proton. In addition, H_2-solvated CH_5^+ has been observed on the very same machine as that for the Yeh–Price–Lee experiment,[38,39] lending further support to our belief that the $C_2H_5^+\cdots H_2$ isomer should be present in this experiment. The only weakness in this argument is the curious absence of the H–H stretch fundamental in the experimental spectra, which fade out just past the anticipated 4116 cm^{-1} prediction. However, as we have demonstrated, other assignments appear to us less justified.

The pressure-independent bands between 3600 and 4200 cm^{-1} are likely to be vibrational excitations of the lowest-energy (bridged) isomer, due to their pressure independence. Our CPMD simulations of the bridged structure did produce intensity near 3600 cm^{-1} due to a combination/overtone band or bands, while the open isomer did not produce peaks in this region. The experimental C–H stretch peaks between 2900 and 3200 cm^{-1} (which did not lead to dissociation without the second laser) are also assigned to this isomer, appearing nicely in the CPMD and HFF predicted spectra.

The most difficult aspect of the spectrum is the 2500–2900 cm^{-1} region. We do not observe a large red-shifting of C–H stretch fundamentals for either the bridged or the solvated-ion isomers. Only the open isomer offers a fundamental in this region, namely one between 2600 and 2800 cm^{-1} (Figure 5). We do see combination/overtone intensity from the CPMD simulations for the bridged and solvated-ion isomers between 2600 and 2800 cm^{-1} but not the five sharp peaks evident in the experimental spectra. Since these peaks are pressure-dependent, we think it unlikely that they are due to the bridged structure. Since they are sharp and act in tandem with the peak at 3964 cm^{-1} and since our solvated-ion CPMD simulations place intensity in this region, their assignment to the solvated-ion isomer, rather than the open isomer, is probably more reasonable.

An infrared determination of the combination/overtone bands of bare $C_2H_5^+$ would be very useful and could well resolve the dilemma posed by the Yeh–Price–Lee spectrum.

Conclusions

$C_2H_7^+$ is predicted to have three isomers at cold temperatures: a bridged (σ_{C-C}-protonated) isomer with two internal rotation modes, an open (σ_{C-H}-protonated) isomer with two internal rotation modes, and a loose $C_2H_5^+\cdots H_2$ solvated-ion isomer. This solid prediction has opened the possibility for reinterpretation of many experimental results. Particularly, the high-energy isomer in the experiments both of Hiraoka and Kebarle[24] and by Yeh, Price, and Lee[25] is more likely to be the solvated-ion isomer rather than the open isomer, contrary to most previous beliefs.[3,4,24,25] The assignment of the solvated-ion isomer to the disappearing peaks in the Yeh–Price–Lee experiment is in agreement with Obata and Hirao,[3] but now based on the stronger evidence supplied in this work. The open isomer (with a 3-center–2- electron CHH bond) may be rare for this ion due to its hanging-well nature and may still be experimentally unknown.

Discrepancies with experiment are still serious, however, and further experiments are needed to resolve them. In particular, experimentally determined IR spectra of $C_2H_5^+$ and additional experimental determinations of the binding energy of $C_2H_5^+\cdots H_2$ would be especially pertinent. Substantial progress has been made here in explaining the mysterious features of the Yeh–Price–Lee spectra; in particular, bridging-proton overtone and combination bands may help explain the peaks between 2500 and 2900 cm^{-1} and between 3600 and 4200 cm^{-1}, including the peak at 3964 cm^{-1}, which is a strong indicator of the presence of the solvated- ion isomer. The 4 kcal mol^{-1} binding energy determined by Hiraoka and Kebarle for their high-energy isomer appears to be too large.

Acknowledgment. Z.F.L. and J.S.T. gratefully acknowledge the financial support for this work by the RGC (The Research Grants Council of the Hong Kong SAR Government, Earmarked Grant Project No. CUHK 4188//97P). P. R. Bunker, J. K. G. Watson, D. D. Klug, and M. Berasconi are all thanked for valuable discussions.

References and Notes

(1) Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716.
(2) Kolbuszewski, M.; Bunker, P. R. *J. Chem. Phys.* **1996**, *105*, 3469.

(3) Obata, S.; Hirao, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3271.

(4) Carneiro, J. W. d. M.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F., III; Rauk, A.; Sorensen, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 3483.

(5) East, A. L. L.; Bunker, P. R. *J. Mol. Spectrosc.* **1997**, *183*, 157.

(6) East, A. L. L.; Kolbuszewski, M.; Bunker, P. R. *J. Phys. Chem. A* **1997**, *101*, 6746.

(7) Tse, J. S.; Klug, D. D.; Laasonen, K. *Phys. Rev. Lett.* **1995**, *74*, 876.

(8) Boo, D. W.; Liu, Z. F.; Suits, A. G.; Tse, J. S.; Lee, Y. T. *Science* **1995**, *269*, 57.

(9) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1147.

(10) Tal'roze, V. L.; Lyubimova, A. L. *Dokl. Akad. Nauk SSSR* **1952**, *86*, 909; *Chem. Abstr.* **1953**, *47*, 2590.

(11) Meisels, G. G.; Hamill, W. H.; Williams, R. R. Jr. *J. Chem. Phys.* **1956**, *25*, 790.

(12) Meisels, G. G.; Hamill, W. H.; Williams, R. R., Jr. *J. Phys. Chem.* **1957**, *61*, 1456.

(13) Wexler, S.; Jesse, N. *J. Am. Chem. Soc.* **1962**, *84*, 3425.

(14) Field, F. H.; Franklin, J. L.; Munson, M. S. B. *J. Am. Chem. Soc.* **1963**, *85*, 3575.

(15) Munson, M. S. B.; Franklin, J. L.; Field, F. H. *J. Phys. Chem.* **1964**, *68*, 3098.

(16) Weiner, J.; Smith, G. P. K.; Saunders, M.; Cross, R. J., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 4115.

(17) Abramson, F. P.; Futrell, J. H. *J. Chem. Phys.* **1966**, *45*, 1925.

(18) Ding, A.; Henglein, A.; Lacmann, K. *Z. Naturforsch.* **1968**, *23A*, 780.

(19) Herman, Z.; Hierl, P.; Lee, A.; Wolfgang, R. *J. Chem. Phys.* **1969**, *51*, 454.

(20) Huntress, W. T., Jr. *J. Chem. Phys.* **1972**, *56*, 5111.

(21) Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261.

(22) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808.

(23) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 1251.

(24) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

(25) Yeh, L. I.; Price, J. M.; Lee, Y. T. *J. Am. Chem. Soc.* **1989**, *111*, 5597.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(27) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(28) MOLPRO94 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlöf, R.D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, and P. R. Taylor.

(29) *CPMD 3.0—Car-Parrinello Molecular Dynamics—An ab Initio Electronic Structure and Molecular Dynamics Program*; IBM Research Division, Zurich Research Laboratory, and Max Planck Institut fur Festkorperforschung: Stuttgart, Germany, 1997.

(30) Vanderbilt, D. *Phys. Rev.* **1990**, *B41*, 7892.

(31) Troullier, N.; Martins, J. L. *Phys. Rev.* **1991**, *B43*, 1993.

(32) Troullier, N.; Martins, J. L. *Phys. Rev.* **1991**, *B43*, 8861.

(33) Vanderbilt, D.; King-Smith, R. D. *Phys. Rev.* **1993**, *B48*, 4442.

(34) Resta, R. *Rev. Mod. Phys.* **1994**, *66*, 899.

(35) Schleyer, P. v. R.; Carneiro, J. W. d. M. *J. Comput. Chem.* **1992**, *13*, 997.

(36) Kim, S.-J.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Phys. Chem.* **1993**, *97*, 12232.

(37) Hiraoka, K.; Kudaka, I.; Yamabe, S. *Chem. Phys. Lett.* **1991**, *184*, 271.

(38) Boo, D. W.; Lee, Y. T. *Chem. Phys. Lett.* **1993**, *211*, 358.

(39) Boo, D. W.; Lee, Y. T. *J. Chem. Phys.* **1995**, *103*, 520.

(40) Hiraoka, K.; Kebarle, P. *J. Chem. Phys.* **1975**, *62*, 2267.

(41) Beuhler, R. J.; Ehrenson, S.; Friedman, L. *J. Chem. Phys.* **1983**, *79*, 5982.

(42) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(43) Komornicki, A.; Jaffe, R. L. *J. Chem. Phys.* **1979**, *71*, 2150.

(44) Marx, D.; Parrinello, M. *Z. Phys. D.* **1997**, *41*, 253.

(45) Okumura, M.; Yeh, L. I.; Lee, Y. T. *J. Chem. Phys.* **1988**, *88*, 79.