The ethyl radical: Photoionization and theoretical studies

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(Received 31 January 1989; accepted 21 March 1989)

The ethyl radical has been produced by the F + C₂H₆ reaction, and studied by photoionization mass spectrometry. The adiabatic ionization potential (IP) is found to be 8.117 ± 0.008 eV. The radical and cation have been studied by the G1 level of molecular orbital theory. The calculated adiabatic ionization potential is 8.06 eV. On the basis of both experiment and theory, it is concluded that the cation in its ground state has a bridged structure. The adiabatic value resolves a previous inconsistency involving \( \Delta H^*_0(C₂H₅^+) \) and IP (C₂H₅). Broad autoionizing structures are observed at higher energy. These features can be rationalized as Rydberg states converging to the first excited state \( ^3A^* \) calculated to be at 12.05 eV.

I. INTRODUCTION

Consider the thermochemical equation

\[
\Delta H^*_0(C₂H₅^+) - \Delta H^*_0(C₂H₅) = \text{IP}(C₂H₅),
\]

where IP (C₂H₅) refers to the adiabatic ionization potential. Up to approximately 1980, each of the individual quantities had been separately measured, with error limits of about ± 1 kcal/mol, and the identity was satisfied. The compilation of Rosenstock et al.,
\(^1\) gave \( \Delta H^*_0(C₂H₅^+) = 219 \) kcal/mol, which becomes ~221.8 kcal/mol at 0 K. For \( \Delta H^*_0(C₂H₅) \), the compilation of Glushko et al.
\(^2\) listed 28.4 ± 1.4 kcal/mol, while McMillen and Golden
\(^3\) selected \( \Delta H^*_0(C₂H₅) = 25.9 ± 1 \) kcal/mol, or \( \Delta H^*_0(C₂H₅) = 28.7 ± 1 \) kcal/mol. These quantities imply that the adiabatic IP of C₂H₅ is 8.38 ± 0.07 eV. Houle and Beauchamp
\(^4\) obtained the photoelectron spectrum of the first band of ethyl radical (by pyrolysis of ethyl nitrite). They reported an adiabatic ionization potential of 8.39 ± 0.02 eV, and a vertical IP of 8.51 eV. Earlier, Elder et al.
\(^5\) had studied the ethyl radical by photoionization mass spectrometry. The ethyl radical was generated by pyrolysis from three different precursors—Pb(C₂H₅)₄, Hg(C₂H₅)₂, and sec-butyl nitrite. All three data sets yielded IP (C₂H₅) < 8.4 eV, but these authors noted that the onset of ionization was not as sharp as their other study on methyl radical. However, taken together the prevailing evidence as of ~1980 indicated that the three thermochemical quantities were consistent with one another, providing support for the individual values.

Since that time, there have been revisions in two of the three quantities. Rosenstock et al.
\(^6\) have summarized the more recent studies, and included their photoion−photoelectron coincidence study of C₂H₅I. Their revised value for \( \Delta H^*_0(C₂H₅^+) \) is 218.8 ± 0.5 kcal/mol. Brouard et al.
\(^7\) determined the equilibrium constant for the reaction

\[
\text{H} + C₂H₅ \rightarrow C₂H₅H,
\]

and thence calculated \( \Delta H^*_0(C₂H₅) = 28.36 ± 0.40 \) kcal/mol. These authors also list recommended vibrational frequencies for C₂H₅ from which we calculate \( \Delta H^*_0(C₂H₅) = 31.00 ± 0.40 \) kcal/mol. In summary, \( \Delta H^*_0(C₂H₅^+) \) has been revised downward by 3 kcal/mol, while \( \Delta H^*_0(C₂H₅) \) has been revised upward by 2.5–2.8 kcal/mol, and consequently the predicted adiabatic IP based on these quantities is 8.14 ± 0.03 eV, now significantly lower than the measured values of 8.39–8.4 eV.

This difference probably has structural implications. \textit{Ab initio} calculations
\(^8\) show that the absolute minimum of the potential energy surface of ground state C₂H₅⁺ corresponds to a nonclassical, hydrogen-bridged structure. A classical transition structure lies about 6 kcal/mol higher on the same potential energy surface. The classical form is closer in geometrical structure to neutral C₂H₅, and hence the Franck-Condon factors are expected to be more favorable for ionization to the classical C₂H₅⁺ structure. A plausible inference is that earlier investigators of the ionization potential of C₂H₅ were able to observe the more intense ionization associated with formation of the classical structure, but were unable to detect the weaker ionization anticipated for the nonclassical structure. The problem of detecting weak, low-energy features is obviously exacerbated by hot bands, since one must distinguish between Boltzmann factors and Franck-Condon factors. Most of the prior investigators generated C₂H₅ by pyrolysis, typically at 500–700 °C. More recently, Dyke et al.
\(^9\) obtained the photoelectron spectrum of the first band of ethyl radical both by pyrolysis of azoethane and by the abstraction reaction of F atoms with C₂H₆. The former source produced a broad, unstructured band with possible contaminants, whereas the latter method yielded a cleaner band with vibrational fine structure. From this spectrum, these authors deduced an adiabatic IP of 8.26 ± 0.02 eV. The implication of their work, and direct studies
\(^10\) of the F + C₂H₆ reaction is that the C₂H₅ radicals formed in this fashion have internal energies characteristic of room temperature, the exothermicity of the reaction appearing as vibrational excitation of the HF product.

The lower adiabatic IP obtained by Dyke et al.
\(^9\) (8.26 vs 8.39–8.4 eV) is closer to the revised difference between \( \Delta H_f \) (C₂H₅⁺) and \( \Delta H_f (C₂H₅) \), but there is still a discrepancy of ~0.1 eV (experimentally based). One of the goals of the present research is to use the method of photoionization mass spectrometry on C₂H₅ radicals produced by the F + C₂H₆ reaction to probe the adiabatic IP of C₂H₅, to see
if a lower value is possible. An additional goal is to apply a high level of \textit{ab initio} molecular orbital theory, to the study of this ionization.

Another reason for reexamining the photoionization of ethyl radical is to probe higher states of the cation. This higher energy region was masked in the photoelectron spectrum by the spectra of other decomposition products. The photoionization mass spectrometric studies, while consistently yielding $\lesssim 8.4$ eV for the onset of ionization, displayed very different behavior with the three different precursors above $\sim 9.6$ eV, possibly due to dissociative ionization of the precursor. By using the F + C$_2$H$_6$ reaction for generating C$_2$H$_5^+$, we hoped to have a window of observation of 3.5–4 eV, since dissociative ionization of C$_2$H$_6$ to give C$_2$H$_5^+$ occurs at $h\nu > 12$ eV. The triplet excited state of C$_2$H$_5^+$ is therefore also investigated theoretically.

II. THEORY—METHODS, AND RESULTS

The \textit{ab initio} molecular orbital studies were carried out using the G1 level of theory. This is a composite procedure, in which structures are determined at the MP2/6-31G* level [including all electrons in the correlation procedure, MP2(FULL)] used in the theoretical calculations leading to a final predicted total energy $E_0$. G1 energies have been shown to reproduce known dissociation and ionization energies to an accuracy of $\pm 0.1$ eV for a wide range of compounds.

The G1 method has been applied to the neutral C$_2$H$_5$ radical (doublet), to the ground state singlet C$_2$H$_5^+$ cation, and two excited state triplet C$_2$H$_5^+$ cations. In each case, three structures denoted as C$_s$ (I), C$_s$ (II), and C$_s$ (III) have been examined. The first two are classical structures and the latter is a nonclassical bridged structure. They are shown in Fig. 1. (In some cases a preliminary HF/6-31G* investigation ruled out certain structures and they were not pursued further at the G1 level of theory.) The MP2(FULL)/6-31G* optimized geometrical parameters for all three structures of C$_2$H$_5$ are listed in Table I. Also given in Table I are MP2(FULL)/6-31G* geometries of certain singlet and triplet cation structures. We now discuss the results of the structural study.

For the neutral radical, the C$_s$ (I) structure is found to be slightly more stable (0.15 kcal/mol, MP2(FULL)/6-31G* level) than the C$_s$ (II) structure, in agreement with previous studies by Pacansky and Dupuis who found nearly free rotation about the C–C bond at the Hartree–Fock level with a basis set including polarization functions. The neutralbridged structure is much higher in energy (48.7 kcal/mol, MP2(FULL)/6-31G* level) and was not explored at higher levels of calculations. This is similar to what was reported by Blomberg and Liu.

![Diagram of structures](image)

**TABLE I.** MP2(FULL)/6-31G* geometries and energies.

<table>
<thead>
<tr>
<th>System</th>
<th>Structure</th>
<th>State</th>
<th>C$_s$C$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>C$_s$H$_s$</th>
<th>Energy$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$CCH$_3$</td>
<td>C$_s$ (I)</td>
<td>$^3\Sigma^+$</td>
<td>1.489</td>
<td>1.100</td>
<td>1.093</td>
<td>1.082</td>
<td>$\cdots$</td>
<td>111.9</td>
<td>$\cdots$</td>
<td>108.1</td>
<td>117.2</td>
<td>128.4</td>
<td>168.3</td>
<td>$\cdots$</td>
<td>78.844/66(0)$^*$</td>
</tr>
<tr>
<td></td>
<td>C$_s$ (II)</td>
<td>$^3\Pi$</td>
<td>1.489</td>
<td>1.091</td>
<td>1.097</td>
<td>1.082</td>
<td>1.081</td>
<td>111.5</td>
<td>121.8</td>
<td>120.8</td>
<td>106.4</td>
<td>$\cdots$</td>
<td>128.0</td>
<td>$\cdots$</td>
<td>78.844/62(1)</td>
</tr>
<tr>
<td></td>
<td>C$_s$ (III)</td>
<td>$^3\Sigma^+$</td>
<td>1.484</td>
<td>1.502</td>
<td>1.082</td>
<td>$\cdots$</td>
<td>60.4</td>
<td>$\cdots$</td>
<td>118.5</td>
<td>$\cdots$</td>
<td>120.5</td>
<td>$\cdots$</td>
<td>78.766/69(1)$^*$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Bond lengths in Å, bond angles in degrees, energies in hartrees.

$^*$ Number of negative frequencies indicated in parentheses from MP2(FULL)/6-31G* calculation unless noted.

$^*$ HF/6-31G* frequency calculation at HF/6-31G* optimized geometry.
For the singlet C₂H₅⁺ cation, the lowest MP2/6-31G* energy is obtained for the nonclassical bridged structure, C₂v (III), as reported previously by Raghavachari et al., Zawarzuck et al., and Lischka and Kohler. No minimum is found for the classical structure C₁ (I) which optimizes at the MP2(FULL)/6-31G* level directly to C₂v (III). The C₁ (I) has a minimum within its imposed symmetry, but this is actually only a saddle point (one negative vibrational frequency) when all degrees of freedom are considered. In fact, the C₁ (II) structure appears to be the transition structure for the scrambling of the protons in the bridged cation.

For ionization to the triplet C₂H₅⁺ cation, the electron can be removed from either a σ(a') or π(a")-type of orbital. In terms of Koopman's theorem using HF/6-31G* orbital energies, the latter ionization is favored. In this study we have considered both possibilities and have optimized the two resulting triplet states for the three types of structures (Fig. 1) that we considered for the singlet cation. For ionization from the π-type orbital of C₂H₅ (resulting in a 3A \(^\prime\) state) the most stable structure is C₁ (I) with the geometrical parameters given in Table I. The electron comes primarily from the CH₂ group and results in a considerable lengthening of two of the CH bond distances and a decrease in the corresponding CHCI angle. The other two structures [C₁ (II) and C₂v (III)] were found to be saddle points on the potential energy surface (HF/6-31G* level) and were not investigated further. For ionization from the σ-type orbital of C₂H₅ (resulting in a 3A \(^\prime\) state) the most stable structure is again C₁ (I) with the geometrical parameters given in Table I. This structure is characterized by a considerable lengthening of the C-C bond (0.36 Å relative to C₂H₅ neutral). It is also more stable than the 3A \(^\prime\) state by 2.6 kcal/mol at the MP2(FULL)/6-31G* level, although this is reversed at higher levels of calculation (see below and Table II). The other two structures [C₁ (II) and C₂v (III)] were investigated and found to be higher in energy. Surprisingly, the bridged structure for this triplet cation is only 8.9 kcal/mol less stable than the classical form at the MP2(FULL)/6-31G* level, but a frequency calculation at the HF/6-31G* level indicated that it was a saddle point. Only the C₁ (I) structure for the 3A \(^\prime\) state was considered at the higher levels of calculation.

The calculations leading to the total G1 energies are listed in Table II. These were done at the stationary points on the MP2/6-31G* surface and also on the C₂H₅⁺ system at the geometry corresponding to the equilibrium structure of the neutral radical C₁ (I). The latter was carried out to get a theoretical value for the vertical ionization energy of C₂H₅.

G1 energies relative to the ground state of ethane are listed in Table III and compared with some experimental data. (Theoretical values for ethane, ethylene, and hydrogen are taken from Ref. 11). These show that the theory gives a good description of the endothermicity of the elimination of H₂ from C₂H₆. They also show a theoretical value of 100.5 kcal/mol for the dissociation energy D₀ of the C-H bond in ethane. This is in satisfactory agreement with the value deduced from \(\Delta H^0_0\) (C₂H₅) due to Brouard et al., both significantly higher than that based on the heats of formation recommended by McMillen and Golden. It is interesting to note that the G1 method gives D₀(CH₂-H) = 103.6 kcal/mol and hence a value of 3.1 kcal/mol for the stabilization comparison

\[ C₂H₅ + CH₄ \rightarrow C₂H₆ + CH₃ \]

G1 theoretical ionization energies are listed in Table IV. These show a predicted adiabatic potential of 8.06 eV for ionization to the nonclassical bridged cation. Ionization to the C₁ (II) structure (which is not a local minimum) requires 8.33 eV. The vertical ionization potential (with no correction for zero-point vibrations) is found to be 8.54 eV. Ionization to the lowest triplet cation (3A \(^\prime\)) is predicted to require 12.05 eV. The higher level corrections (see Table II) make the other triplet state, 3A \(^\prime\) , 0.15 eV less stable than the 3A \(^\prime\) state. The implications of these results will be discussed after presentation of new experimental data.

### III. EXPERIMENTAL ARRANGEMENT

The basic photoionization mass spectrometric apparatus has been described previously. The reactor used for generating C₂H₅ is identical to the device employed for pro-

### TABLE II. Energies and corrections.a

<table>
<thead>
<tr>
<th>System</th>
<th>Structure</th>
<th>State</th>
<th>MP4/6-31G**</th>
<th>(\Delta E(+))</th>
<th>(\Delta E(2df))</th>
<th>(\Delta E(QCI))</th>
<th>(\Delta E(HLC))</th>
<th>(\Delta(ZPE)^b)</th>
<th>(E_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂CCH₂</td>
<td>C₁ (I) 3A (^\prime)</td>
<td>-78.944 59</td>
<td>-1.68</td>
<td>-37.65</td>
<td>-2.04</td>
<td>-37.03</td>
<td>56.38</td>
<td>-78.966 61</td>
<td></td>
</tr>
<tr>
<td>H₂CCH₂</td>
<td>C₁ (II) 3A (^\prime)</td>
<td>-78.944 35</td>
<td>-1.71</td>
<td>-37.75</td>
<td>-2.07</td>
<td>-37.03</td>
<td>56.00</td>
<td>-78.966 91</td>
<td></td>
</tr>
</tbody>
</table>

a Energies in a.u. and corrections in millihartrees.
b Scaled HF/6-31G* zero-point energies.
c Imaginary frequency not included.
d Without the \(\Delta(ZPE)\) correction the C₁ (I) structure is more stable by 0.08 millihartrees (0.05 kcal/mol) which is consistent with the frequency calculation reported in Table I indicating that the C₁ (II) structure is a saddlepoint. The \(E_0\) values indicate that the C₁ (II) structure is more stable due to its imaginary frequency which is not included in \(\Delta(ZPE)\). In the relative energy calculations of Tables III and IV the \(E_0\) for the C₁ (I) structure is used.

Calculation at geometry of neutral radical.
TABLE III. Relative energies (at 0 K).

<table>
<thead>
<tr>
<th>System</th>
<th>Theory (kcal/mol)</th>
<th>(eV)</th>
<th>Experiment* (kcal/mol)</th>
<th>(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂CH₂⁺⁺ (1,4⁺⁺) + H + e</td>
<td>381.8</td>
<td>16.56</td>
<td>286.8⁺⁺</td>
<td>12.44⁺⁺</td>
</tr>
<tr>
<td>H₂CH₂⁺⁺ (1,4⁺⁺) + H + e</td>
<td>378.3</td>
<td>16.40</td>
<td>99.6⁺⁺</td>
<td>96.7⁺⁺</td>
</tr>
<tr>
<td>H₂CH₂⁺⁺ (1,4⁺⁺) + H + e</td>
<td>292.6</td>
<td>12.69</td>
<td>99.0⁺⁺</td>
<td>1.34⁺⁺</td>
</tr>
<tr>
<td>H₂CH₂⁺⁺ (1,4⁺⁺) + H</td>
<td>286.4</td>
<td>12.42</td>
<td>96.7⁺⁺</td>
<td>99.0⁺⁺</td>
</tr>
<tr>
<td>H₂CH₂⁺⁺ (1,4⁺⁺) + H</td>
<td>100.5</td>
<td>4.36</td>
<td>30.9⁺⁺</td>
<td>1.34⁺⁺</td>
</tr>
<tr>
<td>H₂CH₂H₂⁺ + e</td>
<td>29.2</td>
<td>1.30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H₂CH₂H₂⁺</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Using ΔHᵣₑₚ(C₂H₆) of −16.34 kcal/mol from Ref. 2.
⁺⁺ Using ΔHᵣₑₚ(C₂H₄⁺⁺) from Rosenstock et al. (Ref. 6).
⁺⁺ This work.
⁺⁺⁺ Using ΔHᵣₑₚ(C₂H₆) from McMillen and Golden (Ref. 3).
⁺⁺⁺⁺ Using ΔHᵣₑₚ(C₂H₆) from Brouard et al. (Ref. 7).
⁺⁺⁺⁺⁺ Using ΔHᵣₑₚ(C₂H₆) from Ref. 2.

Reducing SiH₆ radicals.¹⁸ Fluorine atoms, produced in a microwave discharge through pure F₂ gas, flow rapidly through a delivery tube. A small fraction enters a reaction cup, to which C₂H₆ has been introduced. After a few collisions, the produced species are allowed to pass through an orifice and enter the photoionization chamber. The fast-flowing fluorine is trapped by a downstream cryopump.

Since the ion signals were weak, especially in the region near threshold, most of the experiments were conducted using only the peak light intensities in the many-line spectrum of molecular hydrogen.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

An overview of the photoion yield curve of C₂H₅⁺ (C₂H₅⁺) is shown in Fig. 2. Somewhere in the region of ~1510 Å a weak signal appears above background. The relative photoionization cross section begins to increase significantly, and roughly linearly, between ~1490–1410 Å. The region between ~1400–1300 Å is relatively flat; below 1300 Å, the cross section increases further, and approximately linearly to about 1200 Å. At still shorter wavelengths, there is evidence of broad, undulating structure, with peaks at ~1205 Å, ~1120 Å and possibly at ~1160 and ~1140 Å. The photoion yield curve declines below ~1120 and attains a minimum at ~1070 Å. Below ~1070 Å, the apparent ion yield curve begins to increase more rapidly. This is presumably due to "leakage," or incomplete mass separation of m/e = 29, C₂H₅⁺, from the tail of the very strong m/e = 30, C₂H₆⁺ (the parent ion of ethane), which has its onset at ~1078 Å. From the known photoion yield curve of C₂H₅⁺ (C₂H₄⁺) and its measured leakage at the m/e = 29 position (determined in a separate experiment), it is possible to subtract this contribution, at least over a limited wavelength range. This is also indicated in Fig. 2. However, at shorter wavelengths (≤1040 Å) other contributions to m/e = 29, from C₂H₅⁺ (C₂H₆⁺) and ¹³C¹₂CH₄⁺ (C₂H₆⁺) have to be taken into account, and begin to dominate the relatively weak photoion signal of C₂H₅⁺ (C₂H₅⁺). The fact that the hydrogen many-line light source does not have strong lines below ~1050 Å limits the accuracy of this subtraction procedure, especially at the shorter wavelengths.

The region of the photoion yield curve near threshold is shown on a magnified scale in Fig. 3. Although the decline toward the background level is monotonic, the data indicate changes of slope, rather like rounded steps. No peaks (which would be characteristic of autoionization) are evident. The plausible inference is that this pattern is a manifestation of direct ionization. The idealized pattern for a vibrational progression in a single vibrational mode would be a staircase structure, with more-or-less constant step width (corresponding to the vibrational frequency being excited) and variable step height (corresponding to the Franck–Condon factor for this mode). The idealized step-like structure would be expected to be rounded, as observed in other cases¹⁹,²⁰ presumably due to rotational effects.

There is no assurance that only a single vibrational progression is to be expected. From the available evidence (calculation for C₂H₅⁺, calculation and experiment for C₂H₅⁺), we anticipate an ionizing transition from a classical, ethane-like structure for C₂H₆ to a hydrogen-bridged, nonclassical structure for C₂H₅⁺. The photoelectron spectrum obtained by Dyke et al.⁹ displays a partially resolved vibrational pattern, which has been interpreted as a progression in a single vibrational mode.

Dyke et al.⁹ report a vertical IP of 8.51 ± 0.01 eV, an

TABLE IV. Ionization energies (in eV at 0 K) from G1 level of theory.

<table>
<thead>
<tr>
<th>System</th>
<th>G1 theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅⁺⁺ (1,4⁺⁺) + e</td>
<td>12.20</td>
<td>8.117 ± 0.008⁺⁺</td>
</tr>
<tr>
<td>C₂H₄⁺⁺ (1,4⁺⁺) + e</td>
<td>12.05</td>
<td>8.26 ± 0.02⁺⁺</td>
</tr>
<tr>
<td>C₂H₅⁺⁺ (1,4⁺⁺) + e</td>
<td>8.33</td>
<td>0.00</td>
</tr>
<tr>
<td>C₂H₅⁺⁺ (1,4⁺⁺) + e</td>
<td>8.06</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* This work.
⁺⁺ Reference 9.
adiabatic IP of 8.26 ± 0.02 eV, and a vibrational spacing of 400 ± 30 cm⁻¹. We have indicated by arrows the location of their vibrational peaks in Fig. 3. There is a rough correspondence between the changes of slope in the photoion yield curve and the position of the arrows, at 8.36 eV = 1483 Å, 8.31 eV = 1492 Å, and 8.26 eV = 1501 Å. At shorter wavelengths, the statistical accuracy improves, but the superposition of several rounded steps begins to blur the distinction between steps. What does seem clear from the larger magnification of Fig. 3 is that the photoion yield has not yet reached the background level at the position of the arrow (1501 Å) corresponding to the adiabatic onset measured by Dyke et al.⁹ The data support the presence of a lower threshold, by perhaps three vibrational quanta (if we assume the same vibrational spacing found by Dyke et al.). The lowest distinct step occurs at 1527.5 ± 1.5 Å = 8.117 ± 0.008 eV, and is weak. This value is in agreement with the predicted value of 8.06 eV from the G1 level of theory (see Table IV). Between 1519–1501 Å (8.16–8.26 eV), there is a relatively large increase in photoion yield (vide infra).

Dyke et al.⁹ have already discussed the difference between their photoelectron spectrum of C₂H₅, in which the radical was produced by the F + C₂H₆ reaction, and other photoelectron spectroscopic studies of C₂H₅⁴⁻⁵ in which the radical was generated by pyrolysis of a precursor (azoethane, n-propyl nitrite). In brief, the experiments employing a pyrolytic source did not reveal meaningful vibrational fine structure, whereas the F + C₂H₆ reaction did. Also, the pyrolytic sources appeared to be plagued by impurity bands overlapping the band attributed to the ethyl radical.

Here, we shall compare the earlier photoionization mass spectrometric studies⁵ of C₂H₅ using pyrolytic sources, with the present work. Elder et al.⁶ already noted that their onset of ionization for C₂H₅ was not as sharp as their other study on CH₃. From their published spectra, the background baseline is not well established, and hence the significance of a weak tail at threshold cannot be assessed. In one of their three spectra, there appears to be evidence for a shallow slope extending to about 8.2 eV, but this was a comparatively "hot" source, and Boltzmann population of excited vibrational levels may have been contributing. There is a rough correspondence between the photoion yield curve in two of their data sets (pyrolysis of diethyl mercury and sec-butyl nitrite) and the present work. Their curves display a quasi-linear increase in ion yield between ~8.4–9 eV, and a relatively flat region between ~9–9.8 eV, beyond which dissociative ionization of the precursor appears to overwhelm the contribution due to primary ionization of C₂H₅. This can be compared to our roughly linear region between ~1490–1410 Å, and a plateau between ~1400–1300 Å. There is
even a hint of rounded step structure near threshold from the sec-butyl nitrite source. However, the implication from all three of their pyrolytic sources is that the signal-to-noise level near threshold was insufficient to establish the presence of a shallower, but significant photoionization cross section near threshold. Also, the data above ~10 eV are inconsistent, and cannot be used to infer any information about a possible excited ionic state.

Dyke et al.\textsuperscript{9} have presented a brief interpretation of the vibrational fine structure in their photoelectron spectrum, which probably manifests itself as the rounded step structure in the present photoion yield curve. An elaboration of this interpretation follows. Present, as well as previous, theoretical calculations indicate that the ethyl radical has a $C_2v$ (I) structure with nearly free rotation about the C–C bond. This $C_2v$ (I) structure of the ethyl radical is similar to the classical structures, $C_2v$ (II) and $C_2v$ (I), of the singlet ethyl cation. However, the classical structures are not local minima on the potential surface, although the $C_2v$ (II) structure is a stationary point. The equilibrium structure of the ethyl cation is a bridged nonclassical structure, $C_{2v}$ (III), the only local minimum on the potential surface. The similarity in geometrical structure between ethyl radical and the classical ion form implies that the most probable transition (maximum Franck–Condon factor, vertical IP) involves a transition to a portion of the ionic potential surface close to that of the classical ion structure. The transition probability for the nonclassical ion structure (adiabatic IP) should be much smaller. One or more vibrational progressions, characteristic of one or more normal modes of the singlet ionic potential surface, should describe the decline in the cross section from the vertical to the adiabatic IP. In principle, the active vibration(s) should be totally symmetric.

The major difference in geometry between the ethyl radical and the classical ion $C_2v$ (II) is a contraction of the C–C bond, from 1.489 to 1.414 Å. As one moves along the potential surface of the cation to the nonclassical structure, $C_{2v}$ (III) the C–C bond decreases further, to 1.380 Å. Hence, a vibrational progression involving the C–C stretching frequency could be excited in the photoionization process. Pacansky and Schrader\textsuperscript{21} report this frequency to be totally symmetric ($a'$) and to have a frequency of 1138 cm$^{-1}$ in the neutral radical. It would likely be still larger in the ion, which has a significantly shorter C–C distance.

The other major geometrical change occurs on the potential surface of the cation, between the classical and nonclassical forms. One way of describing this change is that a hydrogen atom from the CH$_3$ group migrates to the bridging position. The problem is identifying this motion in terms of some normal mode, and correlating it with the observed (400 ± 30 cm$^{-1}$) vibrational progression. The vibrational frequencies of ethyl radical have been reported from theory and experiment, by Pacansky and Schrader,\textsuperscript{21} and calculated by us at the MP2/6-31G* level (See Table V). Apart from the torsional mode (believed to be freely rotating), there are only three experimental frequencies below 1000 cm$^{-1}$, a CH$_3$ umbrella vibration (540 cm$^{-1}$), a CH$_2$–CH$_3$ rocking motion (713 cm$^{-1}$) and a CH$_3$ rocking motion (948 cm$^{-1}$). Dyke et al.\textsuperscript{9} attempted to estimate the frequencies of the cation from the known values for the neutral radical. They chose the lowest (540 cm$^{-1}$) frequency, arguing that it is the mode which corresponds to the transition from a bridged ion to a classical eclipsed ion, and is reduced to ~400 cm$^{-1}$ in the ion. In our judgment, the CH$_3$ umbrella motion does not provide the path between classical and nonclassical ionic structures; it should rather involve a hydrogen atom on the CH$_3$ moiety. This could involve the 948 cm$^{-1}$ frequency (CH$_3$ rock), drastically reduced in the ion.

Rather than using the frequencies of the neutral radical, and guessing the change in these frequencies upon ionization, a more direct approach is to examine the relevant frequencies of the cation's singlet potential surface. The vibrational frequencies of the nonclassical ion structure have been calculated by DeFrees and McLean.\textsuperscript{22} In this paper, we also report (Table V) the theoretical vibrational frequencies corresponding to the classical $C_2v$ (II) ion structure, although (as has already been stated) it does not represent a minimum on the potential surface. Of the 15 frequencies listed by DeFrees and McLean,\textsuperscript{22} the lowest, and the one most likely to represent the transition between classical and nonclassical forms, is designated $b_3$ in $C_{2v}$ geometry, and has been calculated to be 381 cm$^{-1}$ (HF/6-31G*, scaled by a factor of 0.89) and 763 cm$^{-1}$ (MP2/6-31G*, unscaled). Although the calculated 381 cm$^{-1}$ frequency comes closer to the experimental frequency deduced by Dyke et al.\textsuperscript{9} (400 ± 30 cm$^{-1}$), we believe that the calculated 763 cm$^{-1}$ frequency is a more accurate harmonic value.

Consider the motion on the singlet potential surface along this one coordinate, which takes us from the classical to the nonclassical form. In this simplified picture, the nonclassical structure lies in a potential well, ~6 kcal/mol deeper than the classical structure, with no barrier between the two. This well can support several vibrational levels of this single frequency, which can be expected to have strong anharmonicity as the vibrational energy approaches that of the classical structure. Hence, the first one or two vibrational quanta can be expected to be higher (nearer to the calculated value of 763 cm$^{-1}$), but the higher vibrational quanta in this

\begin{table}
\centering
\begin{tabular}{ccc}
\hline
\textbf{C}_2\textbf{H}_5 & \textbf{C}_2\textbf{H}_5^+ & \textbf{C}_2\textbf{H}_3^+ \\
($\textbf{C}_2\textbf{H}_5$) & ($\textbf{C}_2\textbf{H}_5^+$) & ($\textbf{C}_2\textbf{H}_3^+$) \\
\hline
$\alpha'$ & 465 & 3212 & 838 \\
1031 & 2262 & 1138 \\
1110 & 1619 & 1255 \\
1471 & 1403 & 1309 \\
1538 & 1179 & 1504 \\
1553 & 3320 & 1606 \\
3064 & 1290 & 2960 \\
3153 & 1112 & 3203 \\
3244 & 3334 & 3286 \\
163 & 1173 & 3320 \\
841 & 868 & 1138 \\
1249 & 3210 & 776 \\
1558 & 1522 & 1313 \\
3199 & 1366 & 1441 \\
3352 & 763 & 2977 \\
\hline
\end{tabular}
\caption{MP2(FULL)/6-31G* vibrational frequencies (in cm$^{-1}$).}
\end{table}
mode, characteristic of the motion across the entire potential surface spanning classical and nonclassical forms, could be reduced to the value observed in the photoelectron spectrum at a higher energy, 400 ± 30 cm⁻¹. There is, in fact, some evidence in the threshold region of our photoion yield curve for step structure involving the higher frequency. Below our adiabatic onset at 1527.5 Å there is a long plateau, until 1518 Å; thereafter, the photoion yield curve increases rapidly, and displays a step-like feature at ~1510.5 Å. The initial plateau is much longer than those corresponding to the subsequent steps. A possible interpretation is that the region between 1527.5 and 1510.5 Å corresponds to a single vibrational step, of 730 ± 90 cm⁻¹. A presumed step of 400 cm⁻¹ would occur at 1518 Å, where the photoion yield curve displays the onset of a rapid ascent, rather than a step.

At wavelengths longer than 1527.5 Å (our first distinct step), the photoion yield has a residual tail which reaches the background level at 1540.5 ± 1.5 Å. We attribute this to Boltzmann population (~11%) of the 540 cm⁻¹ frequency in neutral C₂H₅ at ~300 K.

A. The excited (triplet) state of C₂H₅⁺

The adiabatic (first) IP of C₂H₅ corresponds to removal of the unpaired electron. Its value (~8.1 eV) is much lower than the adiabatic IP of C₂H₅ (11.15 eV) or even C₂H₆ (10.5 eV). The second IP involves removal of an electron from a fully occupied orbital, presumably ethane-like. The calculated IP of this first excited state (12.05 eV) is close to the adiabatic IP of C₂H₅ (11.5 eV). There has been considerable discussion about the assignment of this state in C₂H₅⁺ [(1eₐ)⁻¹ vs (3aₜ₁g)⁻¹], with (1eₐ)⁻¹ apparently favored currently. The 1eₐ orbital has σ character; it is C~H bonding and C–C bonding.²⁳ The 3aₜ₁g is C–C bonding. From the theoretical calculations in Sec. II we now identify the first excited state in C₂H₅⁺ as resulting from ejection of an electron from an a* orbital, which may be viewed as a component of a π-like orbital, in the lower symmetry. The geometrical structure of this first excited state is given in Table I. Comparison of this structure with that of the neutral C₂H₅ reveals that this ionization process results in a decreased C–C bond length (1.489–1.426 Å), an increase in length of two C–H bonds on the CH₃ side (1.093–1.178 Å), and a decrease in the H–C–H bond angle (108°–66°). This is just the kind of behavior expected for an electron ejected from the 1eₐ orbital in ethane. The prevailing evidence supports the interpretation that the first excited (triplet) state in C₂H₅⁺ is formed by single electron ejection from an orbital which is very similar to the uppermost occupied orbital in C₂H₅, both in bonding behavior and ionization potential. This conclusion is analogous to that found in the photoionization of vinyl radical.²⁰,²¹ There, the first excited (triplet) state of C₂H₅⁺ was identified with single electron ejection from an orbital very similar to the uppermost occupied orbital in C₂H₅ with an IP (10.7 eV) close to that in ethylene (10.5 eV).

In the photoionization study of vinyl radical, several sharp autoionizing features were observed, sufficient to establish a rough value for the convergence limit. In the present study of the ethyl radical, the features are much broader, and any attempt at determining a convergence limit from these features would be more hazardous. Instead, we shall assume that the calculated ionization potential for this triplet state is approximately correct, and try to assign the observed autoionizing features in a plausible fashion.

Robin²⁴ has inferred a quantum defect δ of ~1.07 for the 3s-like, first Rydberg state in ethane, and δ = 0.77 for the 3p- and 4p-like Rydberg states. His anticipated range for the p-like Rydberg states is 0.6 < δ < 0.8. From the absorption spectrum of ethyl radical below the first IP, Wendt and Hunziker²⁵ infer δ = 1.02 for the 3s-like orbital, and δ = 0.65 for the 3p-like orbital.

Applying these alternative estimates for δ, and assuming an IP of 12.05 eV, we infer the following ranges for anticipated Rydberg states:

(a) s-like states:
- n = 3: 1445–1477 Å,
- n = 4: 1179–1185 Å,
- n = 5: 1108–1110 Å;

(b) p-like states:
- n = 3: 1293–1331 Å,
- n = 4: 1144–1154 Å,
- n = 5: 1094–1098 Å.

We tentatively assign the initial "significant" increase in photoion yield between ~1490–1410 Å as formation of a 3s-like state although this growth could also be attributed to changing Franck–Condon factors; the subsequent increase beginning at ~1300 Å is identified with formation of a 3p-like state. At still shorter wavelengths, there is an onset at ~1185 Å, identified with a 4s-like state, and another onset at ~1153 Å, assigned to a 4p-like state. The apparent peaks at ~1160 and ~1140 Å may be attributed to vibrational structure on these Rydberg states, possibly connected with the maxima in the corresponding Franck–Condon transitions. There appears to be a pile up, or superposition of higher Rydberg levels at ~1120 Å, below which the photoion yield declines until the influence of the contaminants precludes further analysis. The lack of sharp structure, and the gradual increase of the photoion yield with decreasing wavelength, is suggestive of strong competition from dissociative or predissociative processes.

V. CONCLUSIONS

(1) The adiabatic ionization potential of C₂H₅, prepared by the F + C₂H₅ abstraction reaction, has been measured by photoionization mass spectrometry to be 8.117 ± 0.008 eV. This value is distinctly lower than the previous PIMS value,³ ≤8.4 eV and also lower than the best PES value,⁹ 8.26 ± 0.02 eV. The presently obtained value is now in agreement with the expectation based on ΔH_f⁰ (C₂H₅) and ΔH_f⁰ (C₂H₅⁺), which it will be recalled was 8.14 ± 0.03 eV. It is also in agreement with the theoretical adiabatic ionization potential of 8.06 eV obtained in the present work. This is consistent with D₀ (C₂H₅-H) = 99.6 ± 6 kcal/mol.

(2) There is a region of weak ascent in the photoion yield curve from the adiabatic threshold to ~1490 Å, below
which a steeper ascent ensues. The weak ascent is attributed to low Franck-Condon factors connecting neutral $\text{C}_2\text{H}_5$ with the bridged, nonclassical structure of $\text{C}_2\text{H}_5^\bullet$. The steeper ascent is identified with the gradual formation of a classical $\text{C}_2\text{H}_5^\bullet$. It is not clear which portion of the steeper ascent is to be identified with "the classical structure." The onset ($\sim 1490 \,\AA$) would correspond to $\sim 4.7$ kcal/mol between classical and nonclassical structures, whereas the midrise of the steep ascent ($\sim 1454 \,\AA$, perhaps the center of the Franck-Condon distribution for formation of the classical structure) would correspond to an energy gap of $\sim 9.5$ kcal/mol between these structures. This is consistent with the theoretical energy difference of 6.2 kcal/mol between the nonclassical and classical structures, the latter being a saddlepoint on the potential energy surface.

(3) Some broad, undulating features are observed at higher photon energy. They are attributed to autoionizing Rydberg states, converging to a higher ionization potential. There is insufficient definition to establish a convergence limit, but these features can be plausibly assigned to $3s$, $4s$, $3p$, and $4p$-like Rydberg states converging to an ionization limit at about 12.05 eV, the latter a calculated value. The excited ionic state is calculated to be a triplet, formed by single electron ejection from an $a^\pi$ orbital similar to the $1e_g$ uppermost occupied orbital in ethane.

ACKNOWLEDGMENTS

This research was supported by the U. S. Department of Energy (Office of Basic Energy Sciences) under Contract No. W-31-109-Eng-38, and the National Science Foundation (Grant No. CHE-84-09405). We wish to thank Dr. C. A. Mayhew and Dr. M. Schwarz for assisting with some of the experimental data acquisition.