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Ionization Energy of Methylene Revisited: Improved Values for the Enthalpy of Formation of CH_2 and the Bond Dissociation Energy of CH_3 via Simultaneous Solution of the Local Thermochemical Network

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The appearance energy of the CH_2^+ fragment from CH_2CO has been carefully remeasured and fitted by a model curve, producing $EA_0(CH_2^+/CH_2CO) = 13.743 \pm 0.005$ eV. This value can be sequentially propagated through selected thermochemical cycles to yield individual values for $EI(CH_2)$, $D_0(H-CH_2)$, $\Delta H°_{f\,0}(CH_2)$, and $\Delta H°_{f\,0}(CH_2CO)$. A set of values with a statistically larger weight is produced by analyzing a local thermochemical network, which combines the present measurement with thirteen other experimental determinations from the literature and encompasses the enthalpies of formation of CH_3, CH_3^+, CH_2, CH_2^+, and CH_2CO. The recommended simultaneously adjusted thermochemical values are: $\Delta H°_{f\,0}(CH_3) = 35.86 \pm 0.07$ kcal/mol (35.05 ± 0.07 kcal/mol at 298 K), $\Delta H°_{f\,0}(CH_3^+) = 262.73 \pm 0.06$ kcal/mol (261.83 ± 0.06 kcal/mol at 298 K), $\Delta H°_{f\,0}(CH_2) = 93.18 \pm 0.20$ kcal/mol (93.31 ± 0.20 kcal/mol at 298 K), $\Delta H°_{f\,0}(CH_2^+) = 332.92 \pm 0.19$ kcal/mol (333.04 ± 0.19 kcal/mol at 298 K), $\Delta H°_{f\,0}(CH_2CO) = -11.10 \pm 0.21$ kcal/mol (-11.85 ± 0.21 kcal/mol at 298 K), as well as $D_0(H_3C-H) = 103.42 \pm 0.03$ kcal/mol (104.99 ± 0.03 kcal/mol at 298 K), $D_0(H_2C-H) = 108.95 \pm 0.20$ kcal/mol (110.35 ± 0.20 kcal/mol at 298 K), $D_0(H_2C{=}CO) = 77.08 \pm 0.02$ kcal/mol (78.73 ± 0.02 kcal/mol at 298 K), $EI(CH_3) = 9.3830 \pm 0.0005$ eV, and $EI(CH_2) = 10.3962 \pm 0.0036$ eV. These values are in excellent agreement with current and several previous experimental measurements. The recommended enthalpy of formation of CH_2 implies that the reaction of singlet methylene with water is essentially thermoneutral (to within ±0.2 kcal/mol) at 0 and 298 K, and slightly endothermic (0.5 ± 0.2 kcal/mol) at 1000 K.

1. Introduction

Accurate and reliable experimental thermochemical values are crucial in developing realistic models of chemical processes. They are also used as benchmarks to test and develop state-of-the-art high-level ab initio calculations, some of which are now capable of achieving sub-kcal/mol accuracy for small systems.

When coupled to meticulous photoionization measurements, the positive ion thermochemical cycle can deliver accurate experimental bond dissociation energies.[1] The approach can be generically illustrated via

$$ABC \rightarrow A + BC \qquad \Delta H°_{r\,0}(1) = D_0(A - BC) \tag{1}$$

$$ABC \rightarrow A + BC^+ + e^- \qquad \Delta H°_{r\,0}(2) = EA_0(BC^+/ABC) \tag{2}$$

$$BC \rightarrow BC^+ + e^- \qquad \Delta H°_{r\,0}(3) = EI(BC) \tag{3}$$

where $D_0(A - BC)$ is the desired spectroscopic (0 K) bond dissociation energy in some molecule ABC, $EA_0(BC^+/ABC)$ is the 0 K appearance energy (EA) of the fragment ion BC^+ from ABC, and EI(BC) is the adiabatic ($0 \leftarrow 0$) ionization energy (EI) of species BC. Since $\Delta H°_{r\,0}(1) = \Delta H°_{r\,0}(2) - \Delta H°_{r\,0}(3)$, the bond dissociation energy can be determined, at least in principle, as a difference of two quantities, $EA_0(BC^+/ABC)$ and EI(BC). These can be obtained from two complementary photoionization experiments: one performed on ABC and the other on BC. The two measurements differ significantly both in their levels of experimental complexity and in the approaches necessary to extract meaningful thermochemical values. The former aspect reflects the fact that while one species is typically a stable molecule, the other is usually a free radical, and the latter is a manifestation of fundamental differences in the underlying photoionization processes (parent ionization vs fragmentation).

The most recently reported value[2] for the C−H bond dissociation energy in methyl (i.e., the second bond dissociation energy in methane) was obtained from photoionization studies using the cycle

$$CH_3 \rightarrow CH_2 + H \qquad \Delta H°_{r\,0}(4) = D_0(H_2C-H) \tag{4}$$

$$CH_3 \rightarrow CH_2^+ + H + e^- \qquad \Delta H°_{r\,0}(5) = EA_0(CH_2^+/CH_3) \tag{5}$$

$$CH_2 \rightarrow CH_2^+ + e^- \qquad \Delta H°_{r\,0}(6) = EI(CH_2) \tag{6}$$

The proposed bond dissociation energy, $D_0(H_2C-H) = 109.0 \pm 0.3$ kcal/mol, results from new experimental determinations[2] leading to $EA_0(CH_2^+/CH_3) = 15.120 \pm 0.006$ eV and $EI(CH_2) = 10.393 \pm 0.011$ eV. In particular, the value for $EI(CH_2)$ originates from the first direct measurement of this quantity, based on the photoionization spectrum of methylene. In the threshold region, the spectrum displays a prominent steplike onset corresponding to the vibrationless ($0 \leftarrow 0$) transition $CH_2^+\ \tilde{X}\ ^2A_1 \leftarrow CH_2\ \tilde{X}\ ^3B_1$. If the customary approach to interpreting the parent ionization onset were to be used, the midrise of the observed $0 \leftarrow 0$ step structure would be simply equated to the adiabatic EI. This works quite well when the basic assumption, which is that the ion yield in the threshold region is generated

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primarily through direct ionization processes, is not far from the truth. In that case the discrepancy between the true location of the head of the Q branch and the phenomenological midrise of the step is usually quite small and can be ignored in comparison to other sources of experimental error. However, if the ion yield in the threshold region has a significant contribution from rotational autoionization, the interpretation of the parent threshold shape becomes more complex, and the midrise approach may introduce an unwanted error in the extracted EI value.

Such complications were demonstrated recently[3] in the related case of methyl radical, CH_3. There it was shown that the thermally dependent depression of the midrise of the $0 \leftarrow 0$ photoionization step (amounting to $\sim$34 cm^{-1} at 300 K and further increasing at higher temperatures) is a result of rotational autoionization. Using available spectroscopic information on CH_3 and CH_3^+, a model that incorporates both direct ionization and rotational autoionization was constructed, rationalizing the experimental observations.[3] The model also enabled the resolution of the discrepancy between the EI(CH_3) value of 79392 ± 5 cm^{-1} (obtained by Herzberg[4] by extrapolating optical spectra) and the PFI ZEKE value[5] of 79349 ± 3 cm^{-1}, in favor of the latter. The fact that the spectroscopic value[4] seems to be in error was surprising, since it is based on extrapolation of three Rydberg series ($\beta\ ^2A_1'$, $\delta\ ^2A_1'$, and $\gamma\ ^2E''$), at least one of which appears to be quite well characterized ($\gamma\ ^2E''$, $n = 3-8$).

As opposed to the case of methyl,[3] the relative paucity of auxiliary spectroscopic information allowed setting only lower and upper limits to the potential effect of rotational autoionization in methylene.[2] The analysis indicated that the adiabatic EI(CH_2) is higher than the midrise (10.382 ± 0.006 eV) of the $0 \leftarrow 0$ step by at least 4 meV, but probably not more than 18 meV, thus effectively bracketing the ionization energy as 10.386 ± 0.006 eV $\leq$ EI(CH_2) $\leq$ 10.400 ± 0.006 eV. Since no clear objective distinctions between the various possibilities could be made, the proposed value,[2] EI(CH_2) = 10.393 ± 0.011 eV, simply corresponds to the arithmetic average of the upper and lower bound, with an error bar sufficiently large to cover the entire bracketed range. It should be parenthetically noted that this average appears in quite good agreement with EI(CH_2) = 10.396 ± 0.003 eV, derived by Herzberg.[4,6-8] However, a dose of prudence is necessary here, since the latter was based on a an even smaller amount of data than in CH_3: it was obtained by extrapolating the first four members of the nd $^3A_2$ Rydberg series to the ionization limit, where only the lowest member (3d) was rotationally resolved,[4] and the position of the remaining three members was determined from the "first strong band".[7]

In this paper we propose to explore a slightly different approach aimed toward further refinement of the value for EI(CH_2). Consider

$$CH_2CO \rightarrow CH_2 + CO \quad \Delta H^\circ_{r\,0}(7) = D_0(H_2C{=}CO) \qquad (7)$$

$$CH_2CO \rightarrow CH_2^+ + CO + e^- \qquad \Delta H^\circ_{r\,0}(8) = EA_0(CH_2^+/CH_2CO) \qquad (8)$$

Noting that $\Delta H^\circ_{r\,0}(6) = \Delta H^\circ_{r\,0}(8) - \Delta H^\circ_{r\,0}(7)$, one obtains EI($CH_2$) = $EA_0(CH_2^+/CH_2CO) - D_0(H_2C{=}CO)$. The C=C bond dissociation energy in ketene happens to be one of several bond energies known to a very high degree of accuracy. The photodissociation of ketene has been shown both theoretically[9] and experimentally[10-12] to proceed without a barrier on the singlet surface. Chen et al.[12] have very precisely determined the spectroscopic threshold for dissociation of ketene into CO and singlet methylene (CH_2, $\tilde{a}\ ^1A_1$) as 30116.2 ± 0.4 cm^{-1}. Subtracting the well-known value[13] for the $\tilde{a}\ ^1A_1 - \tilde{X}\ ^3B_1$ separation in methylene, $\Delta E = 3156 \pm 5$ cm^{-1}, produces $D_0(H_2C{=}CO) = 26960 \pm 6$ cm^{-1} = 3.3426 ± 0.0006 eV. Since the value of $D_0(H_2C{=}CO)$ is known quite accurately, the knowledge of $EA_0(CH_2^+/CH_2CO)$ gives a direct handle on EI(CH_2). Effectively, this approach trades the interpretation of a (perhaps) complex threshold for parent ionization of CH_2 with a comparably more pervious interpretation of the threshold for the CH_2^+ fragment from ketene.

The appearance energy of the CH_2^+ fragment from CH_2CO was examined previously by McCulloh and Dibeler,[14] who reported $EA_0(CH_2^+/CH_2CO) = 13.729 \pm 0.008$ eV. Combined with $D_0(H_2C{=}CO)$ given above, this produces EI(CH_2) = 10.386 ± 0.008 eV. The resulting value coincides with the lower limit set by the direct study,[2] and would seem to imply that rotational autoionization contributes negligibly to the photoionization threshold region of CH_2. However, closer scrutiny reveals that the reported appearance energy[14] may be slightly too low. In an attempt to avoid autoionization structure complicating the CH_2^+ fragment ion yield curve at shorter wavelength, McCulloh and Dibeler used only the very bottom of the fragment onset, close to the region of the "tail", which extends below the thermochemical threshold and is a direct reflection of the Boltzmanian distribution of the internal energies in the starting neutral molecule.[15] In general, the quasi-exponential nature of the "tail" tends to cause significant subjective errors, since it complicates the search for a "linear" section to be graphically extrapolated in order to obtain the threshold value. In particular, visual inspection can be easily biased by an aspect ratio that favors the height at the expense of the width (such as that used by McCulloh and Dibeler[14]), hence promoting a selection of an onset that is too low. To significantly reduce similar subjective tendencies that interfere with the determination of thermochemically relevant appearance energies, we have in recent years developed a fitting procedure for fragmentation thresholds.[16]

In this paper we examine the ion yield of the CH_2^+ fragment from ketene using our fitting procedure to obtain an accurate value for $EA_0(CH_2^+/CH_2CO)$. The new value for $EA_0(CH_2^+/CH_2CO)$ can then be utilized in conjunction with $D_0(H_2C{=}CO)$ to produce a value for EI(CH_2), which can be sequentially promoted through selected thermochemical cycles to yield $D_0(H-CH_2)$, $\Delta H^\circ_f(CH_2)$ and $\Delta H^\circ_f(CH_2CO)$. The targeted enthalpies of formation and bond energies can be further improved by examining the relevant thermochemical network and employing statistical methods to derive an internally consistent set of recommended thermochemical values. Although the foundation for such statistical treatment has been laid a rather long time ago,[17,18] for some reason the approach has been seldom used in practice. Recently[19] we have successfully used this method to simultaneously adjust the enthalpies of formation for a number of fluorinated compounds. In this paper we will examine the relevant local thermochemical network and use the statistical approach to simultaneously adjust enthalpies of formation for CH_3, CH_3^+, CH_2, CH_2^+, and CH_2CO.

2. Experimental Details

The basic instrumental setup employed in the present studies was recently described elsewhere.[20] The small Ne I, N II, and H I atomic emission lines[21] superimposed on the He Hopfield continuum served as accurate internal wavelength calibration standards. The entrance and exit slits were kept at 300 μm, producing a nominal photon resolution of 0.84 Å (fwhm). All

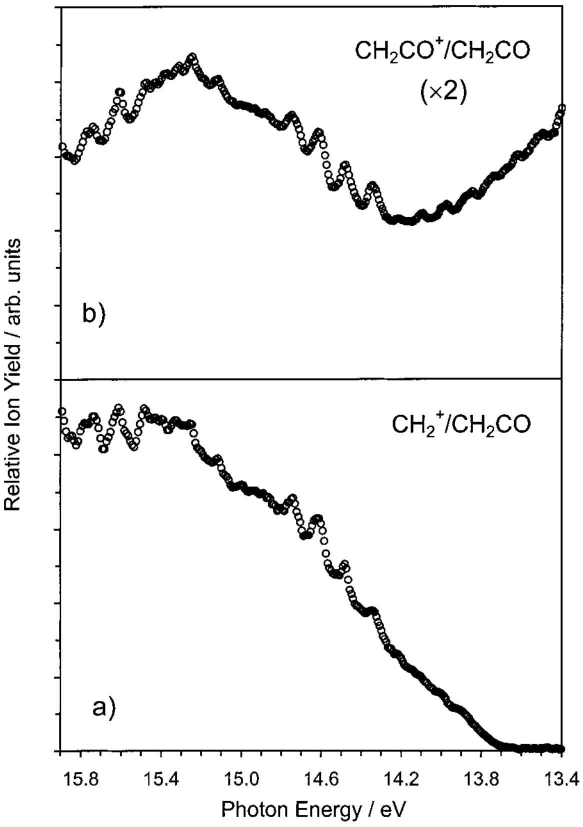

Figure 1. Overview photoionization spectra. (a) Photoionization yield of the CH_2^+ fragment from ketene showing vibrational autoionization structure at higher energy. (b) The relevant section of the parent photoion from ketene, showing a very similar pattern of peaks. Note that the autoionization peaks in the fragment become weaker as one approaches the threshold region.

measurements of light intensity were performed via a copper beryllium photodetector that was calibrated against a sodium salicylate transducer coupled to an external photomultiplier.

Ketene samples were synthesized by a procedure similar to that used by Nuttall et al.[22] The products of pyrolysis of acetic anhydride at ∼880−900 K were passed through a trap at 196 K (dry ice/acetone mixture), which removed water and acetic acid, while ketene was collected at 77 K. The collected product was further purified by several trap-to-trap distillations from 165 K (isobutyl alcohol slush) to 77 K. The pyrolysis of acetic anhydride, as used by Nuttall et al., was found to be a far superior synthetic route to ketene than pyrolysis of diketene (4-methylene-2-oxetanone), which produces a significant (and hard to separate completely) allene impurity.

3. Results

CH_2^+ is the first fragment and the most prominent species in the photoionization spectrum of ketene. Figure 1a shows an overview of its relative fragment ion yield, recorded at 0.05 nm point spacing (equivalent to ∼8 meV in this energy region). Indeed, the fragment ion yield is replete with prominent autoionization peaks, as previously mentioned[14] (but not explicitly shown) by McCulloh and Dibeler. Figure 1b presents the relevant section of the parent ion. Clearly, both species show almost identical patterns of peaks.

The ionic states of ketene are quite well-known from photoelectron spectroscopy.[23−25] This fact helps derive a tentative interpretation of the autoionization structure. The prominent peaks visible both in the parent and the fragment at 14.34_6, 14.48_4, 14.61_4, and 14.74_4 eV, continuing as 14.87_2 and 15.00 eV, form a slightly anharmonic vibrational progression with $\omega_e \sim 1150$ cm^{-1}. They most likely correspond to a Rydberg state with an effective quantum number $n^* \approx 2.81-2.82$, converging to $\tilde{C}\ 2\ ^2B_2$ state of the ketene ion. The progression corresponds to ν_3 (CH_2 scissors), found to be 1087 cm^{-1} in the ion.[23−25] The n^* value matches closely the expected quantum defect $\delta = 1.14$ for an s Rydberg state in atomic oxygen,[26] and hence suggests that this is a 4s $^2B_2$ Rydberg state. The next two members in the same Rydberg series then appear to correspond to the progressions defined by peaks at 15.11_7, 15.24_7, 15.38_0 eV, etc., and again 15.47_5, 15.61_2, 15.74_1 eV, etc. The small peaks below 14.15 eV, clearly visible in the parent ion curve but slightly less pronounced in the CH_2^+ fragment, appear to correspond to higher vibrational members of one or more Rydberg states converging to $\tilde{B}\ 2\ ^2B_1$ state of the ketene ion. Judging from their very small quantum defect ($n^* \approx 3.0$ and 4.0), these would correspond to 3d and 4d Rydberg members.

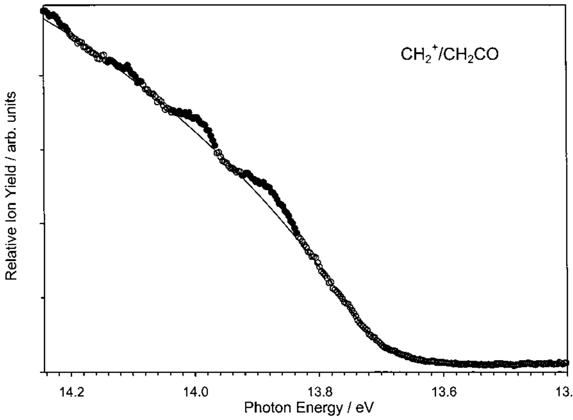

Figure 2. A more detailed view of the threshold region of the CH_2^+ fragment from ketene. Note that autoionization contributes negligibly in the region close to the onset. The solid line is a fit producing $EA_0(CH_2^+/CH_2CO) = 13.743 \pm 0.005$ eV. The points used in the fit are shown as open circles, and comprise all points below 13.83 eV, as well as selected points in the peak valleys at higher energy. Details of the fit are given in the text.

Figure 2 shows in more detail the threshold region of the CH_2^+ fragment, recorded at a point density of 0.02 nm (∼3 meV). The overall shape of the ion yield curve is quite characteristic of a fragment onset, with the exception of four autoionization peaks appearing at energies above 13.8 eV. Although the parent shows rather rich autoionization structure below 13.8 eV, it appears that those Rydberg states contribute negligibly, if at all, to the fragment ion yield. Hence, as already realized by McCulloh and Dibeler,[14] close to its threshold the fragment displays a "clean" region that can be used to determine the onset.

The solid line passing through the data in Figure 2 is a least-squares fit with a threshold model function. The procedure for obtaining appearance energies by fitting experimental ion yield curves with model functions was described in greater detail previously.[16] The kernel function used here has the usual form $\{1 - \exp[-\beta(h\nu - EA_0)]\}$, where $h\nu$ is the photon energy, EA_0 is the 0 K fragmentation threshold, and parameter β adjusts the shape of the kernel function such that it can reproduce the slowing down in the growth of the fragment ion yield toward higher energy. The internal energy distribution of neutral ketene at room temperature was determined using Haarhoff's expression for the density of states[27] and known frequencies.[28] The calculated distribution was used to predetermine the best parameters η and α in $E^{\eta} \exp(-\alpha E)$, with the additional

TABLE 1: Thermochemical Values Directly Derived in the Present Work by Sequential Propagation through Selected Thermochemical Cycles[a]

quantity	0 K	298 K
$EA_T(CH_2^+/CH_2CO)$	13.743 ± 0.005 eV	$[13.685 \pm 0.005]^b$ eV
$IE(CH_2)$	10.400 ± 0.005 eV	10.400 ± 0.005 eV
$D_T(H_2C{-}H)$ to $\tilde{X}\ ^3B_1$ CH_2	$108.8_5 \pm 0.1_8$ kcal/mol	$110.2_5 \pm 0.1_8$ kcal/mol
$D_T(H_2C{-}H)$ to $\tilde{a}\ ^1A_1$ CH_2	$117.8_7 \pm 0.1_8$ kcal/mol	$119.2_5 \pm 0.1_8$ kcal/mol
$\Delta H^\circ_{f\,T}(CH_2, \tilde{X}\ ^3B_1)$	$93.0_6 \pm 0.2_1$ kcal/mol	$93.1_8 \pm 0.2_1$ kcal/mol
$\Delta H^\circ_{f\,T}(CH_2, \tilde{a}\ ^1A_1)$	$102.0_8 \pm 0.2_1$ kcal/mol	$102.1_8 \pm 0.2_1$ kcal/mol
$\Delta H^\circ_{f\,T}(CH_2CO)$	$-11.2_3 \pm 0.2_1$ kcal/mol	$-11.9_7 \pm 0.2_1$ kcal/mol

[a] Auxiliary values used are: $D_0(H_2C{=}CO) = 30116.2 \pm 0.4$ cm^{-1} to form CH_2 a $^1A_1$ from ref 12; $\Delta E(CH_2$ a $^1A_1 - X\ ^3B_1) = 3156 \pm 5$ cm^{-1} from ref 13; $EA_0(CH_2^+/CH_3) = 15.120 \pm 0.006$ eV from ref 2; $\Delta H^\circ_{f\,0}(CH_3) = 35.84 \pm 0.09$ kcal/mol from ref 3; $\Delta H^\circ_{f\,0}(CO) = -27.202 \pm 0.041$ kcal/mol; $\Delta H^\circ_{f\,0}(H) = 51.6336 \pm 0.0014$ kcal/mol from ref 29; vibrational frequencies of CH_2 and CH_3 for $H^\circ_{298} - H^\circ_0$ from ref 47; vibrational frequencies of CH_2CO for $H^\circ_{298} - H^\circ_0$ from ref 28; $H^\circ_{298} - H^\circ_0$ for other species from refs 29 and 31. [b] Value inferred from the fitted EA_0 by subtracting the average vibrational and rotational energy of ketene at 298 K.

requirement that the final function has to reproduce the correct amount of average internal energy available for fragmentation at 298 K (0.058 eV). The data points used in the fit are shown in Figure 2 as open circles. These comprise all points below 13.83 eV, as well as selected points at higher energies in the valleys between the autoionizing peaks. The higher energy points were included in the fit in order to increase leverage over the parameter β of the kernel function, and do not significantly affect the final value for EA_0.

The overall quality of the fit in Figure 2 is quite satisfactory. In particular, the fitted curve is hardly discernible behind the experimental points, and can be followed only in the regions under the autoionizing peaks. The fitted value for the fragment appearance energy is $EA_0(CH_2^+/CH_2CO) = 13.743 \pm 0.005$ eV. Not surprisingly, this value is higher than the onset[14] of 13.729 ± 0.008 eV obtained by McCulloh and Dibeler.

4. Analysis and Discussion

4.1. Direct Thermochemistry. When combined with $D_0(H_2C{=}CO) = 3.3426 \pm 0.0006$ eV given by Chen et al.,[13] the current determination of $EA_0(CH_2^+/CH_2CO) = 13.743 \pm 0.005$ eV produces $EI(CH_2) = 10.400 \pm 0.005$ eV. This ionization energy is congruent with our previously suggested conservative average[2] of 10.393 ± 0.011 eV. In fact, it coincides with the upper limit $EI(CH_2) \leq 10.400 \pm 0.006$ eV derived in the same study by assuming that in the threshold region ($0 \leftarrow 0$) of the $CH_2^+\ \tilde{X}\ ^2A_1 \leftarrow CH_2\ \tilde{X}\ ^3B_1$ transition all Rydberg states with appropriate energy and symmetry can undergo rotational autoionization.

Combining the present $EI(CH_2) = 10.400 \pm 0.005$ eV with our[2] $EA_0(CH_2^+/CH_3) = 15.120 \pm 0.006$ eV yields the second bond dissociation energy in methane, $D_0(H{-}CH_2) = 4.720 \pm 0.008$ eV $= 108.85 \pm 0.18$ kcal/mol (see Table 1), in excellent agreement with the previous[2] determination of 109.0 ± 0.3 kcal/mol. Using[3] $\Delta H^\circ_{f\,0}(CH_3) = 35.84 \pm 0.09$ kcal/mol and[29−31] $\Delta H^\circ_{f\,0}(H) = 51.6336 \pm 0.0014$ kcal/mol yields $\Delta H^\circ_{f\,0}(CH_2) = 93.06 \pm 0.21$ kcal/mol, again in excellent agreement with our previous[2] determination of 93.2 ± 0.3 kcal/mol. The present value for $\Delta H^\circ_{f\,0}(CH_2)$, together with $D_0(H_2C{=}CO)$ of Chen et al.[13] and the well-known[29−31] $\Delta H^\circ_{f\,0}(CO) = -27.202 \pm 0.041$ kcal/mol, can be used to obtain $\Delta H^\circ_{f\,0}(CH_2CO) = -11.23 \pm 0.21$ kcal/mol, equivalent to -11.97 ± 0.21 kcal/mol at 298 K. This route may appear to be somewhat circuitous, since $D_0(H_2C{=}CO)$ was used to obtain $EI(CH_2)$ leading to $\Delta H^\circ_{f\,0}(CH_2)$, which is then combined again with $D_0(H_2C{=}CO)$ to get $\Delta H^\circ_{f\,0}(CH_2CO)$. In fact, the net equivalent of this path does not involve either $D_0(H_2C{=}CO)$ or $\Delta H^\circ_{f\,0}(CH_2)$ and corresponds to a direct comparison of processes (5) and (8), yielding $\Delta H^\circ_{f\,0}(CH_2CO) = EA_0(CH_2^+/CH_3) - EA_0(CH_2^+/CH_2CO) + \Delta H^\circ_{f\,0}(CH_3) + \Delta H^\circ_{f\,0}(CO) - \Delta H^\circ_{f\,0}(H)$.

The enthalpy of formation of ketene has a very interesting history. The NIST Chemistry WebBook[32] lists three values for $\Delta H^\circ_{f\,298}(CH_2CO)$, apparently in inverse chronological order: a 1986 value of -20.85 kcal/mol from Orlov et al.,[33] a 1971 value of -11.4 ± 0.4 kcal/mol from Nuttall et al.,[22] and a 1934 value of -14.78 kcal/mol from Rice and Greenberg.[34]

The result of Rice and Greenberg,[34] derived from calorimetric measurements of enthalpies of reactions of ketene with dilute sodium hydroxide and several aliphatic alcohols, has been subsequently criticized by Nuttall et al.,[22] who demonstrated serious inconsistencies in the older work and have also shown that the value is too low to accommodate photodecomposition of ketene observed routinely to occur at the Hg triplet (365.0, 366.0 and 366.3 nm) and even at wavelengths as long as 369.0 nm.[35]

The work by Nuttall et al.[22] is a very careful calorimetric determination of the enthalpy of reaction of ketene with aqueous sodium hydroxide, resulting in $\Delta H^\circ_{r\,298}(9) = -49.75 \pm 0.38$ kcal/mol for

$$CH_2CO\ (g) + NaOH\ (aq, 500\ H_2O) \rightarrow CH_3CO_2Na\ (aq, NaOH\ soln) \quad (9)$$

Using[36,37] $\Delta H^\circ_{f\,298}(NaOH, aq, 500\ H_2O) = -112.256$ kcal/mol and $\Delta H^\circ_{f\,298}(CH_3CO_2Na, aq, 500\ H_2O) = -173.407$ kcal/mol, and assuming that $\Delta H^\circ_{r\,298}(10) \approx 0$ for

$$CH_3CO_2Na\ (aq, 500\ H_2O) + NaOH\ (aq, 500\ H_2O) \rightarrow CH_3CO_2Na\ (aq, NaOH\ soln) \quad (10)$$

Nuttall et al.[22] obtain $\Delta H^\circ_{f\,298}(CH_2CO) = -11.4 \pm 0.4$ kcal/mol.

The newer work by Orlov et al.[33] is based on combining various positive ion thermochemical cycles with estimations of key thermochemical quantities. They derive several values for the enthalpy of formation of ketene (−17.71, −21.98, −24.21, −20.85 kcal/mol), and select −20.85 kcal/mol as an *upper limit*. Their inferences are difficult to analyze critically, since Orlov et al. show no photoionization spectra and do not elaborate on how they determine the onsets. However, it is quite clear that their proposed value is too low, since with any reasonable values for $\Delta H^\circ_f(CH_2)$ it would imply that the photodissociation of ketene does not commence until ∼330−340 nm.

Most recently Aubry et al.[38] derived the enthalpy of formation of ketene at 298 K as -12.9 ± 1.2 kcal/mol. Their value is based on an electron-impact determination of fragmentation of phenyl acetate producing $C_6H_5OH^+$ and ketene, reported as 9.83

± 0.05 eV at room temperature. This is then combined with $\Delta H°_{f\,298}(C_6H_5OCOCH_3) = -66.8 \pm 0.3$ kcal/mol and $\Delta H°_{f\,298}(C_6H_5OH^+) = 172.6(\pm0.3)$ kcal/mol from Lias et al.[39] to produce the reported value for $\Delta H°_{f\,298}(CH_2CO)$. Although it is not clear how Aubrey et al.[38] corrected their result for the internal energy of phenyl acetate available for fragmentation,[40] if at all, their value appears to nominally agree quite well with the theoretical number by Scott and Radom,[41] who recommend −12.4 kcal/mol as the "best" value, based on a combination of G2, G2(MP2), G2//MP2/6-311+G(2df,p), CBS-Q, and CBS-APNO results. For comparison, both G2 and G3 produce[42,43] −12.1 kcal/mol.

Of the four experimental determinations of $\Delta H°_{f\,298}(CH_2CO)$ discussed above, the calorimetric value by Nuttal et al.[22] of $\Delta H°_{f\,298}(CH_2CO) = -11.4 \pm 0.4$ kcal/mol corresponds to the most careful measurements and clearly stands on very firm ground. The enthalpy of formation of ketene suggested by the present measurement, −11.97 ± 0.21 kcal/mol, agrees quite well with their determination. In fact, since the error bars of the two values overlap within a rather narrow range, one may be tempted to suggest that the "best" value for the enthalpy of ketene at 298 K is probably close to −11.7 to −11.8 kcal/mol.

4.2. Thermochemical Network. Rather than attempting to find overlapping uncertainties between various proposed values, the proper approach to obtaining the "best" thermochemical values is by constructing a thermochemical network and analyzing it via statistical methods.[17,18] Topologically, the vertices (nodes) of such a network represent thermochemical properties, such as enthalpies of formation, of a group of related molecules. The edges (links) between the nodes consist of various experimental measurements, such as enthalpies of reaction, bond dissociation energies, etc. The network maps onto a set of linear algebraic equations, where each equation corresponds to one of the topological edges, while the unknowns correspond to the vertices of the network. The network is overdetermined if the number of edges (equations) exceeds the number of vertices (unknowns). In principle, the thermochemical network encompasses the whole known universe of thermochemical properties and all related experimental measurements. In practice, only a "local" network, encompassing properties of a very limited subset of related compounds, is considered. To be tractable, the local network has to be cautiously disconnected from the global network. This can be achieved by carefully selecting a set of "auxiliary" thermochemical properties that can be assumed to be "known" and essentially unaffected by the links present in the local network. The optimal solution of the network is found by a least-squares fit in an error-weighted space. Error weighting reflects the very nature of experimental data, which are always subject to experimental uncertainties. The degree to which the reported uncertainty reflects the true uncertainty of the measurement is generally quite nonuniform, and may depend on the meticulousness of the experimentalist, his awareness of possible sources of systematic errors, etc. Hence, linear error weighting appears more appropriate than square.[18] In addition, the least-squares fit of the network is preceded by a thorough linear analysis of the network, which evaluates the overall consistency of the network and helps identify measurements that either have unrealistically tight uncertainties or may require reexamination/reinterpretation. A more complete account of the network approach, including the mathematical methods used, was given recently.[19]

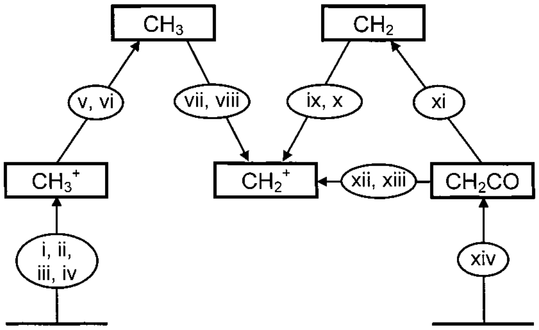

Figure 3. Schematic representation of the topology of the thermochemical network considered in the present paper. The rectangles denote the 0 K enthalpies of formation. The numbers in ovals refer to links listed in Table 2. The network maps onto an overdetermined set of fourteen algebraic equations with five unknowns.

Figure 3 depicts schematically the network considered in this paper. The nodes consist of 0 K enthalpies of formation of CH$_3$, CH_3^+, CH_2, CH_2^+, and CH_2CO. Table 2 lists the fourteen relevant experimental determinations initially considered as links within the network. The first four links, (i) through (iv), correspond to determinations[2,14,44,45] of $EA_0(CH_3^+/CH_4)$. Since $\Delta H°_{f\,0}(H) = 51.6336 \pm 0.0014$ kcal/mol and $\Delta H°_{f\,0}(CH_4) = -15.925 \pm 0.072$ kcal/mol are well established,[29,31] it is quite safe to assume that these values will not be affected by solving the local network. Hence, links (i) through (iv) effectively serve the purpose of anchoring one side of the network to the absolute scale. The next six links correspond to two of each of the following determinations: adiabatic ionization energy of methyl,[4,5] 0 K appearance energy of the CH_2^+ fragment from methyl,[2,46] and adiabatic ionization energy of methylene.[2,6−8] Link (xi) is a measurement of the spectroscopic C=C bond dissociation energy of ketene to form singlet methylene,[12] coupled to the singlet−triplet splitting in methylene.[13] Link (xii) represents the determination of the 0 K appearance energy of the CH_2^+ fragment from ketene presented in section 3, while link (xiii) is the same quantity as given by McCulloh and Dibeler.[14] In the process of setting up links (v) through (xiii), the only additional assumption that has to be made is that $\Delta H°_{f\,0}(CO) = -27.202 \pm 0.041$ kcal/mol is well known[29] and will not be affected by the present network. The final link corresponds to the calorimetric determination of the enthalpy of formation of ketene by Nuttall et al.[22] Just as they did, we assume that $\Delta H°_{f\,298}(NaOH, aq, 500\ H_2O) = -112.256$ kcal/mol and $\Delta H°_{f\,298}(NaC_2H_3O_2, aq, 500\ H_2O) = -173.407$ kcal/mol are reasonably well determined[37] and that $\Delta H°_{f\,298}(NaC_2H_3O_2, aq, 500\ H_2O) \approx \Delta H°_{f\,298}(NaC_2H_3O_2, aq, NaOH\ soln)$. The potential inaccuracy associated with the latter assumption can be estimated as <0.08 kcal/mol, well within the error bar of their measurement. After inserting the fixed enthalpies of formation, this link produces $\Delta H°_{f\,298}(CH_2CO) = -11.40 \pm 0.41$ kcal/mol, which is then converted to $\Delta H°_{f\,0}(CH_2CO) = -10.65 \pm 0.41$ kcal/mol by using known frequencies[28] to obtain $H°_{298} - H°_0$ for CH_2CO. Hence, link (xiv) anchors the other side of the network to an absolute scale.

The network is highly overdetermined, since it corresponds to fourteen algebraic equations with five unknowns. The initial analysis of the network, which checks the system for overall consistency and includes a variety of linear tests and trial solutions[19] both in unweighted and error-weighted space, reveals a couple of inconsistencies. Not surprisingly, one of them concerns links (v) and (vi), showing that they are mutually incompatible. In particular, link (vi) tends to deviate from the various partial solutions to the remainder of the network by amounts considerably exceeding the stated uncertainty of 5 cm^{-1}. Since it has been previously demonstrated[2] that the EI-

TABLE 2: Reactions Used in Constructing the Local Thermochemical Network[a]

n[b]	reaction	measurement	ref
(i)	$CH_4(g) \rightarrow CH_3^+(g) + H(g) + e^-(g)$	$EA_0(CH_3^+/CH_4) = 14.322 \pm 0.003$ eV	3
(ii)	$CH_4(g) \rightarrow CH_3^+(g) + H(g) + e^-(g)$	$EA_0(CH_3^+/CH_4) = 14.323 \pm 0.001$ eV	44
(iii)	$CH_4(g) \rightarrow CH_3+(g) + H(g) + e^-(g)$	$EA_0(CH_3^+/CH_4) = 14.320 \pm 0.004$ eV	45
(iv)	$CH_4(g) \rightarrow CH_3^+(g) + H(g) + e^-(g)$	$EA_0(CH_3^+/CH_4) = 14.324 \pm 0.003$ eV	14
(v)	$CH_3(g) \rightarrow CH_3^+(g) + e^-(g)$	$EI(CH_3) = 79349 \pm 3\ cm^{-1}$	5
(vi)[c]	$CH_3(g) \rightarrow CH_3^+(g) + e^-(g)$	$EI(CH_3) = 79392 \pm 5\ cm^{-1}$	4
(vii)	$CH_3(g) \rightarrow CH_2^+(g) + H(g) + e^-(g)$	$EA_0(CH_2^+/CH_3) = 15.120 \pm 0.006$ eV	2
(viii)	$CH_3(g) \rightarrow CH_2^+(g) + H(g) + e^-(g)$	$EA_0(CH_2^+/CH_3) = 15.09 \pm 0.03$ eV	46
(ix)	$CH_2(g) \rightarrow CH_2^+(g) + e^-(g)$	$EI(CH_2) = 10.393 \pm 0.011$ eV	2
(x)	$CH_2(g) \rightarrow CH_2^+(g) + e^-(g)$	$EI(CH_2) = 10.396 \pm 0.003$ eV	6−8
(xi)	$CH_2CO(g) \rightarrow CH_2(g) + CO(g)$	$D_0(H_2C{=}CO) = 26960 \pm 6\ cm^{-1}$	12, 13
(xii)	$CH_2CO(g) \rightarrow CH_2^+(g) + CO(g)$	$EA_0(CH_2^+/CH_2CO) = 13.743 \pm 0.005$ eV	present work
(xiii)[d]	$CH_2CO(g) \rightarrow CH_2^+(g) + CO(g)$	$EA_0(CH_2^+/CH_2CO) = 13.729 \pm 0.008$ eV	14
(xiv)[e]	$CH_2CO(g) + NaOH(aq, 500H_2O) \rightarrow CH_3CO_2Na(aq, NaOH\ soln)$	$\Delta H^\circ_{r\,298} = -49.75 \pm 0.38$ kcal/mol	22

[a] The following thermochemical quantities were treated as fixed (i.e., well established from prior considerations and unaffected by the present network): $\Delta H^\circ_{f\,0}(CH_4) = -15.925 \pm 0.072$ kcal/mol from ref 31, $\Delta H^\circ_{f\,0}(H) = 51.6336 \pm 0.0014$ kcal/mol, and $\Delta H^\circ_{f\,0}(CO) = -27.202 \pm 0.041$ kcal/mol from ref 29; $\Delta H^\circ_{f\,298}(NaOH, aq, 500\ H_2O) = -112.256$ kcal/mol, and $\Delta H^\circ_{f\,298}(NaC_2H_3O_2, aq, 500\ H_2O) = -173.407$ kcal/mol from ref 37. [b] Running index of network link. [c] Linear analysis clearly shows that links (v) and (vi) are mutually inconsistent. Prior work (ref 2) has demonstrated that (v) is correct and that (vi) corresponds to an ionization energy of CH_3 that is too high. Hence, this link (vi) has been excluded from the final fit. [d] The error bar on this link has been amplified by 50% after linear analysis. [e] As in ref 22, $\Delta H^\circ_{f\,298}(NaC_2H_3O_2, aq, 500\ H_2O)$ was used as an approximation for $\Delta H^\circ_{f\,298}(NaC_2H_3O_2, aq, NaOH\ soln)$. It can be estimated that the associated error is probably no larger than 0.06−0.08 kcal/mol. After inserting the fixed enthalpies of formation, this link produces $\Delta H^\circ_{f\,298}(CH_2CO) = -11.40 \pm 0.41$ kcal/mol, which corresponds to $\Delta H^\circ_{f\,0}(CH_2CO) = -10.65 \pm 0.41$ kcal/mol.

(CH_3) value[4] in question appears to be too high, it seems reasonable to eliminate link (vi) from the final analysis. This intervention impacts primarily the final error bars: leaving that link in the network produces error bars that are almost uniformly ~3.6 times larger, although it skews the final values only by 0.03_2 kcal/mol or less. Another approach would have been to increase the error bar associated to link (vi) to ~40−45 cm^{-1}, which is roughly the amount by which this link is believed to be in error.[2] At that point, however, it makes very little difference whether this link is left in the network or eliminated. The second incongruity uncovered by the initial analysis is somewhat subtler. It concerns link (xiii), which tends to produce deviations from various partial solutions that exceed the stated uncertainty by 30−50%. Increasing the error bar accordingly can easily alleviate this problem. It should be pointed out that the latter intervention is mostly cosmetic: if the error bar of link (xiii) is left untouched, this leads to final values that differ at most by 0.01_8 kcal/mol and increases the final error bars by ~9−10%.

Finally, we should add that, despite the fact that it is not clear if the result of Aubry et al.[38] contains the appropriate corrections, and that it involves enthalpies of formation of phenyl acetate and phenol cation, we have attempted for the sake of completeness to take it at face value and include it as link (xv). However, because this measurement has a much coarser error bar than any of the other links, its inclusion has a negligible effect on the final results: the values change by 0.01_6 kcal/mol or less, and the error bars generally increase by less than ~3%.

The values for the enthalpies of formation of CH_3, CH_3^+, CH_2, CH_2^+, and CH_2CO at 0 K, obtained by simultaneous least-squares solution to the network in linearly weighted error space, are given in Table 3. The quoted error bars correspond to the customary two standard deviations, and reflect the uncertainty of the fit as well as the uncertainties of the individual links. The enthalpies at 298 K, which are also listed in Table 3, have been derived from the 0 K values by combining directly calculated $H^\circ_{298} - H^\circ_0$ terms for CH_3, CH_3^+, CH_2, CH_2^+, and CH_2CO with tabulated[29−31] $H^\circ_{298} - H^\circ_0$ for the elements in their standard states. Vibrational frequencies for CH_3, CH_3^+, CH_2, and CH_2^+ were taken from Jacox,[47] and, where not known, substituted by scaled (0.8929) frequencies calculated[48] at the HF/6-31G(d) level, while the frequencies for CH_2CO were taken from Moore and Pimentel[28a] and Duncan et al.[28b,c] The stationary (mass spectrometric) electron convention was followed for all ionic species. While this, of course, does not make any difference at 0 K, the values for $\Delta H^\circ_{f\,298}(CH_3^+)$ and $\Delta H^\circ_{f\,298}(CH_2^+)$ corresponding to the thermal electron convention can be simply obtained by adding 1.481 kcal/mol to the 298 K values given in the table. Table 3 also includes several relevant bond dissociation energies and reaction enthalpies. Since the uncertainties of the listed enthalpies are correlated, one should use the full covariance matrix to obtain the uncertainties of derived quantities, such as enthalpies of reaction. In lieu of that approach, the network was reexpressed in terms of bond dissociation energies and ionization energies as unknowns, and solved again. The uncertainties quoted next to the derived quantities correspond to two standard deviations of such solutions.

It is pleasing to note that the values in Tables 1 and 3 are in excellent agreement. The very slight differences in the enthalpies of formation (~0.1_0−0.1_3 kcal/mol) are well within the quoted uncertainties. The main reason for the slight deviations resides in the fact that Table 1 is based on a limited subset of the network depicted in Figure 3. In particular, the values in Table 1 are derived from a selected single path through the network, which uses the closure of the triangle $CH_2CO-CH_2-CH_2^+$ and places the values on an absolute scale by using only one side of the network (i.e., the $CH_3^+-CH_3-CH_2^+$ path). The network solution approach provides a more balanced view, making full use of all the available measurements. These produce multiple paths to the solution, each of which contributes to the adjusted values according to the associated uncertainty. Hence, a simultaneous solution to the network is to be preferred and is the foundation upon which the recommended values in Table 3 rest.

The same reasons betoken that, in the absence of new direct high-resolution measurements of ionization energy of methylene, the value $EI(CH_2) = 10.3962 \pm 0.0036$ eV $= 83951 \pm 29\ cm^{-1}$,

TABLE 3: Recommended Thermochemical Values, Based on the Simultaneous Least-Squares Solution of the Local Thermochemical Network[a]

quantity	0 K	298 K
$\Delta H^\circ_{f\,T}(CH_3)$	35.86 ± 0.07 kcal/mol	35.05 ± 0.07 kcal/mol
$\Delta H^\circ_{f\,T}(CH_3^+)$	262.73 ± 0.06 kcal/mol	261.83 ± 0.06 kcal/mol
$\Delta H^\circ_{f\,T}(CH_2, \tilde{X}\ ^3B_1)$	93.18 ± 0.20 kcal/mol	93.31 ± 0.20 kcal/mol
$\Delta H^\circ_{f\,T}(CH_2, \tilde{a}\ ^1A_1)$	102.21 ± 0.20 kcal/mol	102.31 ±0.20 kcal/mol
$\Delta H^\circ_{f\,T}(CH_2^+)$	332.92 ± 0.19 kcal/mol	333.04 ±0.19 kcal/mol
$\Delta H^\circ_{f\,T}(CH_2CO)$	−11.10 ± 0.21 kcal/mol	−11.85 ± 0.21 kcal/mol
$D_T(H_3C{-}H)$	103.42 ± 0.03 kcal/mol	104.99 ± 0.03 kcal/mol
$D_T(H_2C{-}H)$ to $\tilde{X}\ ^3B_1\ CH_2$	108.95 ± 0.20 kcal/mol	110.35 ± 0.20 kcal/mol
$D_T(H_2C{-}H)$ to $\tilde{a}\ ^1A_1\ CH_2$	117.97 ± 0.20 kcal/mol	119.35 ± 0.20 kcal/mol
$D_T(H_2C{=}CO)$ to $\tilde{X}\ ^3B_1\ CH_2$	77.08 ± 0.02 kcal/mol	78.73 ± 0.02 kcal/mol
$D_T(H_2C{=}CO)$ to $\tilde{a}\ ^1A_1\ CH_2$	86.11 ± 0.01 kcal/mol	87.74 ± 0.01 kcal/mol
$EI(CH_3)$	9.3830 ± 0.0005 eV	−
$EI(CH_2)$	10.3962 ± 0.0036 eV	−
$\Delta H^\circ_{r\,T}[CH_4 \rightarrow CH_2\ (\tilde{X}\ ^3B_1) + H_2]$	109.11 ± 0.20 kcal/mol	111.13 ± 0.20 kcal/mol
$\Delta H^\circ_{r\,T}[CH_4 \rightarrow CH_2\ (\tilde{a}\ ^1A_1) + H_2]$	118.13 ± 0.20 kcal/mol	120.14 ± 0.20 kcal/mol
$\Delta H^\circ_{r\,T}[CH_2\ (\tilde{a}\ ^1A_1) + H_2O \rightarrow CH_3 + OH]$	0.11 ± 0.20 kcal/mol	−0.05 ± 0.20 kcal/mol

[a] Auxiliary values used are: singlet−triplet splitting in CH_2 of 3156 ± 5 $cm^{-1} \equiv 9.023 \pm 0.014$ kcal/mol from ref 13; $\Delta H^\circ_{f\,0}(CH_4) = -15.925 \pm 0.072$ kcal/mol, $\Delta H^\circ_{f\,0}(CO) = -27.202 \pm 0.041$ kcal/mol, and $\Delta H^\circ_{f\,0}(H) = 51.6336 \pm 0.0014$ kcal/mol from ref 31; $D_0(HO{-}H) = 118.08 \pm 0.05$ kcal/mol from ref 1; vibrational frequencies of CH_2, CH_2^+, CH_3, and CH_3^+ for $H^\circ_{298} - H^\circ_0$ from ref 47; vibrational frequencies of CH_2CO for $H^\circ_{298} - H^\circ_0$ from ref 28; $H^\circ_{298} - H^\circ_0$ for other species from refs 29, 30, and 31.

which results from the solution to the network, should be considered as the most current. The value of 10.400 ± 0.005 eV listed in Table 1, although in very good agreement with the recommended value, should be considered subordinate. The currently recommended value is also in very good accord with the coarser average value of 10.393 ± 0.011 eV suggested by our direct study[2] of the photoionization threshold of CH_2, and, in fact, is clearly closer to the upper limit (≤ 10.400 ± 0.006 eV) than to the lower limit (≥ 10.386 ± 0.006 eV) set by the same study. The lower limit assumed that rotational autoionization has an insignificant contribution to the shape of the photoionization threshold of methylene, while the upper limit went to the other extreme and assumed that all Rydberg states which are energetically allowed and have proper symmetry do autoionize and contribute to the shape of the ionization threshold. In the direct study,[2] we have also considered an intermediate model, which assumed that rotational autoionization is K_a-preserving, and that only the $K_a = 0$ stack is active, leading to $\Delta N = -2$ mechanism and resulting in a ionization energy of methylene ~8 meV above the nominal midrise, i.e., $EI(CH_2) \approx 10.390$ eV. The basis for these restrictive assumptions originated in optical spectra,[4,8] which tend to suggest that higher K_a stacks are completely wiped out by predissociation, at least in the case of lower Rydberg states. The present result would suggest that the truth is somewhere between the intermediate model, which assumes that predissociation wipes out all $K_a > 0$ levels, and the extreme model, which assumes that all levels survive long enough to undergo rotational autoionization. The extreme model has to include the $\Delta N =$ odd mechanism for higher K_a stacks and does not need to assume K_a preservation. While partial predissociation of high Rydberg states seems to be present, it appears that a significant fraction of the levels allowed by energy and symmetry to rotationally autoionize contribute to the shape of the photoionization threshold in methylene. If this is correct, it may imply that for the states in question the predissociation rate and autoionization rate are quite competitive, and while some levels undergo predissociation, at least for some levels rotational autoionization is faster.

It is interesting to note that the presently recommended value for $EI(CH_2)$ happens to be exactly identical to Herzberg's[7] 83851 cm^{-1}, reported elsewhere[4,8] slightly incongruously as 83857 cm^{-1} and 10.396 ± 0.003 eV. It should be also noted that the values for $EI(CH_3) = 79348.9 \pm 4.4$ cm^{-1} and $D_0(CH_2CO) = 26960.7 \pm 8.8$ cm^{-1} are within <1 cm^{-1} of the precise measurements by Blush et al.[5] (79349 ± 3 cm^{-1}) and Chen et al.[12] (26960 ± 6 cm^{-1}). Although these measurements were used as inputs while constructing the network, and both end up being solitary links between the two relevant nodes, whether their values will be preserved in the simultaneous solution depends on the influence of the other links in the network. Clearly, the high weight (low uncertainty) of links (v) and (xi) helps to keep them unchanged but is also suggestive that the rest of the network does not contain grossly incongruent links.

The enthalpies of formation of CH_3, CH_3^+, CH_2 (triplet and singlet), and CH_2^+, the bond dissociation energies $D_0(H{-}CH_3)$ and $D_0(H{-}CH_2)$, and the related enthalpies of reaction of singlet methylene with water and H_2 elimination from CH_4 listed in Table 3 are in excellent agreement with our previous recommendations[2,3] and should be regarded as their further refinement. In addition, the enthalpy of formation of ketene suggested by the present work (−11.8 ± 0.2 kcal/mol at 298 K) is in excellent agreement with the determination by Nuttall et al.,[22] who obtained −11.4 ± 0.4 kcal/mol. Both the older value of −14.78 kcal/mol from Rice and Greenberg,[34] and the newer value of −20.85 kcal/mol from Orlov et al.[33] are very clearly too low. The recent electron-impact value of −12.9 ± 1.2 kcal/mol also appears somewhat too low, albeit its generous error bar allows for sufficient overlap with the present result.

5. Conclusions

The appearance energy of the CH_2^+ fragment from CH_2CO has been carefully remeasured and fitted by a model curve, producing $EA_0(CH_2^+/CH_2CO) = 13.743 \pm 0.005$ eV, slightly higher than the previous study.[14] When combined with $D_0(H_2C{=}CO) = 3.3426 \pm 0.0006$ eV given by Chen et al.,[13] this leads to $EI(CH_2) = 10.400 \pm 0.005$ eV, in good agreement with the direct study[2] producing 10.393 ± 0.011 eV. Together with previously determined[2] $EA_0(CH_2^+/CH_3) = 15.120 \pm 0.006$ eV, this yields $D_0(H{-}CH_2) = 108.85 \pm 0.18$ kcal/mol, and ultimately $\Delta H^\circ_{f0}(CH_2) = 93.06 \pm 0.21$ kcal/mol. These "direct" values, obtained by sequentially propagating the measured appearance energy of CH_2^+ from ketene through selected thermochemical cycles are listed in Table 1 and are in quite good agreement with previous[2,3,22] determinations. However, a statistically more significant set of values can be produced by analyzing the local thermochemical network based on fourteen experimental determinations. The simultaneous solution to this network produces an improved and internally consistent set of thermochemical values, implying inter alia that the best current value for the ionization energy of methylene is 10.3962 ± 0.0036 eV. The recommended thermochemical values, based on the network are: $\Delta H^\circ_{f\,0}(CH_3) = 35.86 \pm 0.07$ kcal/mol (35.05 ±0.07 kcal/mol at 298 K), $\Delta H^\circ_{f\,0}(CH_2) = 93.18 \pm 0.20$ kcal/mol (93.31 ± 0.20 kcal/mol at 298 K), and $\Delta H^\circ_{f\,0}(CH_2CO) = -11.10 \pm 0.21$ kcal/mol (−11.85 ± 0.21 kcal/mol at 298 K), as well as $D_0(H_3C-H) = 103.42 \pm 0.03$ kcal/mol (104.99 ± 0.03 kcal/mol at 298 K) and $D_0(H_2C-H) = 108.95 \pm 0.20$ kcal/mol (110.35 ± 0.20 kcal/mol at 298 K). These are listed in Table 3, together with several other related values. Since the bond dissociation energy of methyl to produce singlet methylene is extremely close to the bond dissociation energy in water, the reaction of singlet methylene with water, considered important in describing combustion of hydrocarbon fuels, becomes a very sensitive test of the enthalpy of reaction of methylene. With the currently recommended values, this reaction is essentially thermoneutral within the confidence limits (±0.20 kcal/mol), although it appears to be nominally slightly endothermic (0.11 kcal/mol) at 0 K, and slightly exothermic (−0.05 kcal/mol) at room temperature. At higher temperatures the essential thermoneutrality changes to slight endothermicity, amounting to 0.5 ± 0.2 kcal/mol at 1000 K.

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References and Notes

(1) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(2) Litorja, M.; Ruscic, B. *J. Chem. Phys.* **1998**, *108*, 6748.

(3) Litorja, M.; Ruscic, B. *J. Chem. Phys.* **1997**, *107*, 9852.

(4) Herzberg, G. *Proc. R. Soc. London Ser. A* **1961**, *262*, 291.

(5) Blush, J. A.; Chen. P.; Wiedman, R. T.; White, M. G. *J. Chem. Phys.* **1993**, *98*, 3557.

(6) Herzberg, G.; Shoosmith, J. *Nature* **1959**, *183*, 1801.

(7) Herzberg, G. *Can. J. Phys.* **1961**, *39*, 1511.

(8) Herzberg, G.; Johns, J. W. C. *J. Chem. Phys.* **1971**, *54*, 2276.

(9) Allen, W. D.; Shaefer, H. F., III *J. Chem. Phys.* **1988**, *89*, 329. See also: Allen, W. D.; Shaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 2212.

(10) Hayden, C. C.; Neumark, D. M.; Shobatake, K.; Sparks, R. K.; Lee, Y. T. *J. Chem. Phys.* **1982**, *76*, 3607.

(11) Nesbitt, D. J.; Petek, H.; Foltz, M. F.; Filseth, S. V.; Bamford, D. J.; Moore, C. B. *J. Chem. Phys.* **1985**, *83*, 223.

(12) Chen, I.-C.; Green, W. H., Jr.; Moore, C. B. *J. Chem. Phys.* **1988**, *89*, 314.

(13) (a) Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724. (b) Jensen P.; Bunker, P. R. *J. Chem. Phys.* **1988**, *89*, 1327. (c) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251. (d) Leopold, D. G.; Murray, K. K.; Stevens Miller, A. E.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

(14) McCulloh, K. E.; Dibeler, V. H. *J. Chem. Phys.* **1976**, *64*, 4445.

(15) (a) Guyon, P. M.; Berkowitz, J. *J. Chem. Phys.* **1971**, *54*, 1814. (b) Chupka, W. A. *J. Chem. Phys.* **1971**, *54*, 1936.

(16) (a) Ruscic, B.; Berkowitz, J. *J. Phys. Chem.* **1993**, *97*, 11451. (b) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *100*, 4498. (c) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 7795. (d) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 7975. (e) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 10936. (f) Asher, R. L.; Appelman, E. H.; Ruscic, B. *J. Chem. Phys.* **1996**, *105*, 9781. (g) Asher, R. L.; Ruscic, B. *J. Chem. Phys.* **1997**, *106*, 210.

(17) Guest, M. F.; Pedley, J. B.; Horn, H. *J. Chem. Thermodyn.* **1969**, *1*, 345.

(18) Garvin, D.; Parker, V. B.; Wagman, D. D.; Evans, W. H. *Proceedings of the Fifth Biennial International CODATA Conference*; Dreyfus, B., Ed.; Pergamon: Oxford, 1977; p 567.

(19) Ruscic, B.; Michael, J. V.; Redfern, P. C.; Curtiss, L. A.; Raghavachari, K. *J. Chem. Phys. A* **1998**, *102*, 10889.

(20) Litorja, M.; Ruscic, B. *J. Electron Spectrosc.* **1998**, *97*, 131.

(21) Kelly, R. L. Atomic and Ionic Spectrum Lines Below 2000 Å: Hydrogen Through Krypton, *J. Phys. Chem. Ref. Data* **1987**, *16*, Suppl. 1.

(22) Nuttall, R. L.; Laufer, A. H.; Kilday, M. V. *J. Chem. Thermodyn.* **1971**, *3*, 167.

(23) Baker, D.; Turner, D. W. *J. Chem. Soc. D* **1969**, 480.

(24) Hall, D.; Maier, J. P.; Rosmus, P. *Chem. Phys.* **1977**, *24*, 373.

(25) (a) Niu, B.; Bai, Y.; Shirley, D. A. *Chem. Phys. Lett.* **1992**, *201*, 217. (b) Niu, B.; Bai, Y.; Shirley, D. A. *J. Chem. Phys.* **1993**, *99*, 2520.

(26) Theodosiou, C. E.; Inokuti, M.; Manson, S. T. *At. Data* **1986**, *35*, 473.

(27) Haarhoff, P. C. *Mol. Phys.* **1963**, *7*, 101.

(28) (a) Moore, C. B.; Pimentel, G. *J. Chem. Phys.* **1963**, *38*, 2816. (b) Duncan, J. L.; Ferguson, A. M.; Harpper, J.; Tonge, K. H. *J. Mol. Spectrosc.***1987**, *122*, 72. (c) Duncan, J. L.; Ferguson, A. M.; Harpper, J.; Tonge, K. H. *J. Mol. Spectrosc.* **1987**, *125*, 196.

(29) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(30) (a) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1. (b) Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, 4th ed.; *J. Phys. Chem. Ref. Data* **1998**, Monograph No. 9.

(31) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; Hemisphere: New York, 1989.; Vols. 1 and 2.

(32) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, November 1998; (http://webbook.nist.gov).

(33) Orlov, V. M.; Krivoruchko, A. A.; Misharev, A. D.; Takhistov, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2619. See also the English translation: Orlov, V. M.; Krivoruchko, A. A.; Misharev, A. D.; Takhistov, V. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, 2404.

(34) Rice, F. O.; Greenberg, J. *J. Am. Chem. Soc.* **1934**, *56*, 2268.

(35) Laufer, A. H., unpublished results quoted by Nuttal and al. (ref 22).

(36) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. *NBS Technol. Note 270−3*, **1968**. (Note that the relevant values are the same as in Reference 37.)

(37) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(38) Aubry, C.; Holmes, J. L.; Terlouw, J. K. *J. Phys. Chem. A* **1997**, *101*, 5958.

(39) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L., Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(40) Aubry et al., ref 38, do not attach a temperature either to their measured values or to the derived thermochemical results, other than stating that "the apparatus and sample inlet operated at room temperature". They measured by electron-impact the following fragmentation process: $C_6H_5OCOCH_3 \rightarrow C_6H_5OH^+ + CH_2CO$ and reported 9.83 ± 0.05 eV. It would appear that they simply combined this value together with what corresponds to 298 K enthalpies of formation of $C_6H_5OCOCH_3$ and $C_6H_5OH^+$ (from ref 39) to produce the enthalpy of formation of ketene. (By using the values that Aubry et al. provide, rounding them off to the nearest kJ/mol, and using the above "procedure", we can exactly reproduce their $\Delta H^\circ_f(CH_2CO) = -54$ kJ/mol $= -12.9$ kcal/mol.) If the enthalpy of the fragmentation reaction at some temperature T, $\Delta H^\circ_{r\,T}$, were known, then indeed one could write $\Delta H^\circ_{f\,T}(CH_2CO) = \Delta H^\circ_{r\,T} + \Delta H^\circ_{f\,T}(C_6H_5OCOCH_3) - \Delta H^\circ_{f\,T}(C_6H_5OH^+)$. Assuming that there was no kinetic shift involved, the spectroscopic (0 K) fragmentation threshold, $EA_0(C_6H_5OH^+/C_6H_5OCOCH_3)$, would correspond to $\Delta H^\circ_{r\,0}$ for the above fragmentation reaction and, when combined with $\Delta H^\circ_{f\,0}(C_6H_5OCOCH_3)$ and $\Delta H^\circ_{f\,0}(C_6H_5OH^+)$, could yield $\Delta H^\circ_{f\,0}(CH_2CO)$. However, the fragmentation threshold extrapolated from an experiment conducted at room temperature (298 K) does not simply correspond to the enthalpy of the fragmentation reaction at 298 K, $\Delta H^\circ_{r\,298}$. Rather, it corresponds to the 0 K threshold lowered by the available internal energy of $C_6H_5OCOCH_3$, $<E(C_6H_5OCOCH_3)>_{vib+rot,298}$ (see, for example, ref 15). A kinetic shift would tend to counter this effect and push the observable onset toward higher energy. However, from an analysis of the metastable peak, Aubrey et al. conclude that the kinetic shift is negligibly small. Hence, $EA_{298}(C_6H_5OH^+/C_6H_5OCOCH_3) = \Delta H^\circ_{r\,0} - <E(C_6H_5OCOCH_3)>_{vib,298} - 1.5kT$. On the other hand, $\Delta H^\circ_{r\,298} = \Delta H^\circ_{r\,0} - <E(C_6H_5OCOCH_3)>_{vib,298} + <E(C_6H_5OH^+)>_{vib,298} + <E(CH_2CO)>_{vib,298} + 4kT$. Equating $\Delta H^\circ_{r\,298} = EA_{298}(C_6H_5OH^+/C_6H_5OCOCH_3)$, which is apparently what Aubrey et al. did, leads to cancellation of the $<E(C_6H_5OCOCH_3)>_{vib,298}$ term (∼3.5−4 kcal/mol), but leaves an error amounting to $<E(C_6H_5OH^+)>_{vib,298} + <E(CH_2CO)>_{vib,T} + 5.5kT \approx 5.5$ kcal/mol, which is about 4.5 times larger than their quoted error bar. However, this

can be offset if, by some reason, the extrapolated appearance potential is higher than the thermochemical $EA_{298}(AB^+/ABCD)$. Both a nonnegligible kinetic shift and the notorious tendency for electron impact to produce appearance potentials that are too high, would act in the right direction and bring about a fortuitous cancellation of errors.

(41) Scott, A.; Radom, L. *Int. J. Mass Spectrom. Ion Processes* **1997**, *160*, 73. See also: Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

(42) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(43) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(44) Weitzel, K. M.; Malow, M.; Jarvis, G. K.; Baer, T.; Song, Y.; Ng, C.-Y. *J. Chem. Phys.*, submitted for publication.

(45) Chupka, W. A. *J. Chem. Phys.***1968**, *48*, 2337.

(46) Chupka, W. A.; Lifshitz, C. *J. Chem. Phys.* **1967**, *48*, 1109.

(47) Jacox, M. E. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*; J. Phys. Chem. Ref. Data* **1994**, Monograph 3.

(48) 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.; M. Al-Laham, 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 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.