The ionization potentials of CH₄ and CD₄

J. Berkowitz, J. P. Greene, and H. Cho
Argonne National Laboratory, Argonne, Illinois 60439

B. Rusčić
Argonne National Laboratory, Argonne, Illinois 60439 and Rugjer Bosković Institute, Zagreb, Yugoslavia

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The adiabatic ionization potential of CD₄ is measured by photoionization mass spectrometry to be 12.65 ± 0.015 eV, which is 0.05 ± 0.02 eV higher than that of CH₄. The difference is attributed to zero point energy differences, rather than different Jahn–Teller stabilization energies.

The purpose of this work is to address (and hopefully to correct) some inconsistencies in the literature regarding the ionization potentials of CH₄ and CD₄.

Numerous authors have pointed out that the tetrahedral structure of neutral methane becomes distorted in the lowest state of the methane cation. The lowest energy ionization process involves removal of an electron from a filled t₂ orbital, resulting in a triply degenerate state which displays distortions involving vibronic interaction, and described by the Jahn–Teller theorem. As a consequence of these distortions, one can anticipate an extended Franck–Condon region in the ionization process. The adiabatic ionization potential may be difficult or impossible to access.

A measure of this difficulty is the range of adiabatic ionization potential values reported by photoionization mass spectrometry and photoelectron spectroscopy (earlier electron impact measurements are ignored here). These values range from 12.55 ± 0.05 to 12.78 eV; Rabalais et al. infer that "...it is quite certain that the adiabatic ionization potential of methane is below 12.616 eV, and probably lies near 12.51 eV."

Three groups, representing a subset of the above authors, have also measured the adiabatic ionization potential of CD₄. In each case, the value for CD₄ is significantly larger than for CH₄ (12.88 ± 0.008/12.704 ± 0.008; 12.87 ± 0.02/12.71 ± 0.02; 12.83/12.75 eV). Several explanations for this discrepancy suggest themselves:

(1) The difference in adiabatic thresholds between CH₄ and CD₄ is a manifestation of zero point energy differences.

(2) The Jahn–Teller splitting in CH₄⁺ and CD₄⁺ results in slightly different energies of the most stable distorted states.

(3) The Franck–Condon factors for the adiabatic transitions in CH₄ and CD₄ are both very low. The difference in reported thresholds is a measure of the lower Franck–Condon factor, and hence greater difficulty in measuring the adiabatic IP of CD₄ than of CH₄.

Points (1) and (2) have been addressed in a recent ab initio calculation by Paddon–Row et al., although it was not their primary motivation. They calculated the vibrational frequencies of the ground states of CH₄⁺ and CD₄⁺ (both Cᵥ), and hence their zero point energies. They obtained 25.1 kcal/mol for CH₄⁺, 18.4 kcal/mol for CD₄⁺. The zero point energies of the ground states of CH₄ and CD₄ can be obtained from well-known experimental frequencies, and are 27.10 and 20.10 kcal/mol, respectively. From these numbers, one can compute IP (CD₄⁺) − IP (CH₄⁺) = 0.013 eV, a difference much smaller than reported by the three groups cited above.

However, in the absence of experimental frequencies for the cations, a more plausible calculation of zero point energies would involve the use of a consistent set of calculated frequencies, in which the calculations have been performed at the same level of accuracy. Such a set of frequencies is available at the Hartree–Fock 6-31 G* level for CH₄⁺ and CD₄⁺. These frequencies yield 30.0, 22.0, 25.1, and 18.4 kcal/mol, respectively, for the zero point energies of CH₄⁺ and CD₄⁺. (Fortuitously, the zero point energies for CH₄⁺ and CD₄⁺ calculated in this way are exactly the same as given by Paddon–Row et al. at the MP2/6-31 G** level). From these frequencies one obtains IP (CD₄⁺) − IP (CH₄⁺) = 0.056 eV. Experience has shown that the frequencies calculated at the Hartree–Fock 6-31 G* level, when multiplied by a factor 0.89, come close to experimental harmonic frequencies. For example, when the calculated frequencies of CH₄⁺ are adjusted by this factor, the comparison with experiment is as follows (calculated/experimental) in cm⁻¹: 1324/1306; 2939/3018.7; 1516/1534; and 2845/2916.5. Hence, if we apply this factor to the zero point energies, we obtain IP (CD₄⁺) − IP (CH₄⁺) = 0.050 eV.

Paddon–Row et al. appear to have explored the potential surface of CH₄⁺, together with various deuterated substituents, over an extended geometric range without calling attention to possible different geometries or stabilities for the Jahn–Teller split ground states of CH₄⁺ and CD₄⁺. We infer that their calculations lead to the same structures and stabilities for both ions (static Jahn–Teller effect).

To clarify the experimental situation, we have measured the threshold region of the photoionization spectrum of CD₄, and concurrently remeasured the photoionization spectrum of CH₄. The latter study was previously reported from this laboratory, using a different apparatus. Both CD₄ and CH₄ were cooled to 78 K prior to photoionization. The pressure of the target gas (indirectly measured in the external vacuum chamber) was made the same in both cases, and
the intensity of the CD$_4^+$ signal was within 20% of the CH$_4^+$ signal at $>13$ eV. The results near threshold are shown in Figs. 1(a) and 1(b).

The photon yield curve for CH$_4^+$ [Fig. 1(a)] is essentially the same as was obtained here earlier, and compatible with the measured photoelectron spectrum of Rabalais et al. (see Fig. 64 of Ref. 14). The observed threshold occurs at $983 \pm 1$ Å, $= 12.61 \pm 0.01$ eV, and is not influenced by temperature. There is a characteristic succession of curved steps, presumably signaling the onset of successive vibrational levels of CH$_4^+$. The ratio of step heights of the second step to the first is $\leq 3$.

The photoion yield curve for CD$_4^+$ [Fig. 1(b)] displays a very weak tail, or curved step, between $\sim 971$–$980$ Å. The ratio of step heights of the second step to this first step is $\sim 5$. In order to examine possible experimental artifacts, such as collisional ionization of high Rydberg states which could result in ionization below the ionization threshold, we have examined the ratio of the intensity at the tail ($971$–$980$ Å) to that of the higher energy portion of the curve and to the background at still longer wavelengths, all as a function of target gas pressure. Collisional ionization would presumably vary as the square of pressure. The signals in all three energy regions varied linearly with pressure. The background below threshold was partly due to scattered light (independent of measured light intensity) and partly to photoelectrons from surfaces (linearly dependent on measured light intensity). The CH$_4^+$ measurements displayed no “tail,” and hence no collisional ionization, at the relatively low pressures employed in these experiments ($\sim 10^{-5}$ Torr), and therefore we conclude that the tail in the CD$_4^+$ spectrum is real, and represents the first ionization step.

The result of these measurements is that the adiabatic ionization potential of CD$_4$ is $979.5 \pm 1$ Å, $= 12.65 \pm 0.01$ eV, higher than that of CH$_4$. On the basis of the good agreement between the calculated and observed difference in adiabatic ionization potentials, the simplest inference is that this difference is entirely due to zero point energy differences between the deuterated and protonated species. The difference in Jahn–Teller stabilization energies is presumably a still smaller effect.

The Boltzmann distribution of rotational levels in the ground state is expected to smear the onset, and to move the $J^* = 0 \rightarrow J' = 0$ adiabatic value to slightly higher energy than the actual onset. In order to assess the significance of this effect upon the difference in adiabatic ionization potentials of CH$_4$ and CD$_4$, we have performed the following calculation.

The geometrical structure of CH$_4^+$ and CD$_4^+$ was taken to be the C$_4v$ (2) structure given by Paddon-Row et al. From this structure, we compute rotational constants $A = 6.793$ cm$^{-1}$, $B = 6.699$ cm$^{-1}$, and $C = 5.313$ cm$^{-1}$ for CH$_4^+$, and $A = 3.399$ cm$^{-1}$, $B = 3.402$ cm$^{-1}$, and $C = 2.686$ cm$^{-1}$ for CD$_4^+$. For the purposes of this calculation, we treat this as a symmetric rotor, i.e., $A = B = (A + B)/2$. The neutral CH$_4$ (CD$_4$) is a spherical top, whose rotational constants are given by Herzberg, [Ref. 11(a)], p. 456. The latter reference (p. 39) also gives the statistical weights due to nuclear spin. With these parameters, it can readily be shown that at 78 K we need consider rotational quantum numbers only through $J^* = 8$ for CH$_4$ and $J^* = 12$ for CD$_4$.

The rotational energy levels of CH$_4^+$ and CD$_4^+$ were calculated from the equation for a symmetric top [Ref. 11(a), p. 24], and thereupon the transition energies...
(CH₄ → CH₄⁺, etc.), were referenced to the J'' = 0 → J'' = 0 energy, the adiabatic value. Hönln–London factors were evaluated alternatively for a perpendicular or for a parallel transition (Ref. 15, p. 226), although we believe that this is a perpendicular transition. The energies were sorted into a monotonic sequence, and the intensities (taking into account Boltzmann factor, spin statistical weight, Hönln–London factor, and a Gaussian shape for the line to represent the slit function) summed successively to simulate step function threshold behavior.

As expected, the resulting curve is s shaped in the cases considered. It is nearly a linearly increasing function up to its maximum, with an exponential rounding near the onset and the maximum. If the linear portion is extrapolated to zero intensity, it departs from the J'' = 0 → J'' = 0 energy by ~43 cm⁻¹ for CH₄⁺ and ~31 cm⁻¹ for CD₄⁺, assuming a perpendicular transition. (The rotationally adiabatic transition occurs at ≤ 1/3 the maximum intensity.) Thus, the difference between the extrapolated onset and the rotationally adiabatic value is ~0.005 eV for CH₄, and ~0.004 eV for CH₄⁺. By choosing the extrapolated onsets, instead of attempting to infer the rotationally adiabatic values, we incur a possible error of ~0.001 eV for the difference in adiabatic ionization potentials for CH₄ and CD₄, well within the statistical uncertainty of the present experiment. The results are approximately the same for the parallel transition. We conclude that rotational effects are too small to influence the present results.

An additional observation is that the Franck–Condod factor for the first vibrational step in the transition CD₄ → CD₄⁺ is weaker than the corresponding one in CH₄. These factors have tended to reinforce one another in prior measurements, making the observed difference in adiabatic ionization potentials larger than the value reported here; 0.178² ± 0.008, 0.16¹ ± 0.02, and 0.08⁸ eV.

The photoelectron spectrum of the first band in CH₄ (CD₄⁺) reported by Brundle et al.⁸ helps to explain the observed adiabatic behavior. This band displays two broad peaks (assigned as Jahn–Teller components) and a shoulder on the high energy side, which may be a third Jahn–Teller state. Although the center of this band remains essentially the same for CH₄ and CD₄, the splitting of Jahn–Teller states is smaller in CD₄⁺ (0.7 eV) than in CH₄⁺ (0.8 eV). Also, the half-width of the entire band is distinctly narrower in CD₄⁺, the ratio of bandwidths being about 1.18.

The vibrations in CH₄ are essentially hydrogenic motions. A comparison of the vibrational frequencies of CH₄ and CD₄ shows that they differ by a factor of approximately √2. It can readily be shown that the classical amplitudes of vibration in the ν'' = 0 states then differ by ~4√2 = 1.189.

The classical turning points roughly define the Franck–Condod width, which should therefore be correspondingly narrower in CD₄. Since one is starting out with a more localized wave function, the Franck–Condod overlap with the adiabatic geometry of the ion is much weaker for CD₄⁺, and hence it is more difficult to measure.

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¹⁸(a) G. Herzberg, Molecular Spectra and Molecular Structure. Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand, Princeton, 1945), Vol. 2; (b) K. S. Kransov, Molokulyarnye Postayannye Neorgani
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¹⁹The calculated frequencies of CH₄ at the Hartree–Fock, 6-31 G* level are given by J. A. Pople, B. T. Luke, M. J. Frisch, and J. S. Binkley, J. Phys. Chem. 89, 2198 (1985). The corresponding frequencies for CD₄, CH₄⁺, and CD₄⁺ have been made available to us by Dr. L. A. Curtiss, Chemical Technology Division, Argonne National Laboratory.