The ionization potentials of CH_4 and CD_4

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

B. Ruscić
Argonne National Laboratory, Argonne, Illinois 60439 and Rugjer Bošković Institute, Zagreb, Yugoslavia

The adiabatic ionization potential of CD_4 is measured by photoionization mass spectrometry to be $12.65_8 \pm 0.015$ eV, which is 0.05 ± 0.02 eV higher than that of CH_4. 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 CH_4 and CD_4.

Numerous authors[1] 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 t_2 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[2–5] and photoelectron spectroscopy[6–10] (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 CD_4. In each case, the value for CD_4 is significantly larger than for CH_4 ($12.882 \pm 0.008/12.704 \pm 0.008$[2]; $12.87 \pm 0.02/12.71 \pm 0.02$[3]; $12.83/12.75_8$ eV). Several explanations for this discrepancy suggest themselves:

(1) The difference in adiabatic thresholds between CH_4 and CD_4 is a manifestation of zero point energy differences.

(2) The Jahn–Teller splitting in CH_4^+ and CD_4^+ results in slightly different energies of the most stable distorted states.

(3) The Franck–Condon factors for the adiabatic transitions in CH_4 and CD_4 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 CD_4 than of CH_4.

Points (1) and (2) have been addressed in a recent *ab initio* calculation by Paddon-Row *et al.*,[1] although it was not their primary motivation. They calculated the vibrational frequencies of the ground states of CH_4^+ and CD_4^+ (both C_{2v}), and hence their zero point energies. They obtained 25.1 kcal/mol for CH_4^+, 18.4 kcal/mol for CD_4^+. The zero point energies of the ground states of CH_4 and CD_4 can be obtained from well-known experimental frequencies,[11] and are 27.10 and 20.10 kcal/mol, respectively. From these numbers, one can compute IP (CD_4) − IP (CH_4) = 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[12] for CH_4, CD_4, CH_4^+, and CD_4^+. These frequencies yield 30.0, 22.0, 25.1, and 18.4 kcal/mol, respectively, for the zero point energies of CH_4, CD_4, CH_4^+, and CD_4^+. (Fortuitously, the zero point energies for CH_4^+ and CD_4^+ 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 (CD_4)–IP (CH_4) = 0.056 eV. Experience has shown[13] 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 CH_4 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 (CD_4) − IP (CH_4) = 0.050 eV.

Paddon-Row *et al.*[1] appear to have explored the potential surface of CH_4^+, 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 CH_4^+ and CD_4^+. 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 CD_4, and concurrently remeasured the photoionization spectrum of CH_4. The latter study was previously reported from this laboratory,[5] using a different apparatus. Both CD_4 and CH_4 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 $\geqslant 13$ 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,[5] and compatible with the *measured* photoelectron spectrum of Rabalais *et al.*
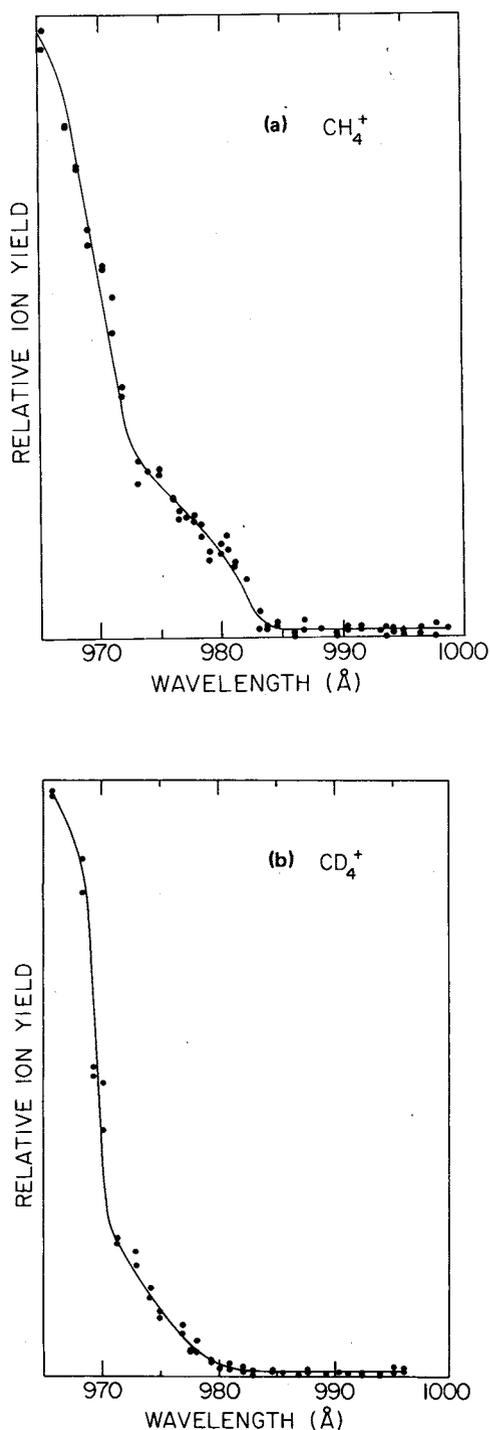

(a) CH$_4^+$

(b) CD$_4^+$

FIG. 1. The photoion yield curves of (a) CH$_4$ and (b) CD$_4$ in the wavelength region near the ionization threshold. Both experiments were performed with the gas cooled to 78 K, and with a wavelength resolution of 0.28 Å (FWHM). The hand-drawn lines through the data points are intended only to guide the eye. They have not been fitted to a particular function.

(see Fig. 64 of Ref. 14). The observed threshold occurs at $983 \, {}^{+\,0}_{-\,1}$ Å $\equiv 12.61 \, {}^{+\,0.01}_{-\,0.00}$ 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 $\lesssim 3$.

The photoion yield curve for CD$_4^+$ [Fig. 1(b)] displays a very weak tail, or curved step, between ~ 971–980 Å. The ratio of step heights of the second step to this first step is ~ 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 ± 1 Å $\equiv 12.65_8 \pm 0.015$ 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_{2v} (2) structure given by Paddon-Row *et al.*[1] 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 $C = 2.668$ cm^{-1} for CD$_4^+$. For the purposes of this calculation, we treat this as a symmetric rotor, i.e., $A \approx B = (A + B)/2$. 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

$(CH_4 \rightarrow CH_4^+$, etc.), were referenced to the $J''= 0 \rightarrow J'' = 0$ energy, the adiabatic value. Hönl–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, Hönl–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 $J'' = 0 \rightarrow J' = 0$ energy by ~ 43 cm^{-1} for CH$_4^+$ and ~ 31 cm^{-1} for CD$_4^+$, assuming a perpendicular transition. (The rotationally adiabatic transition occurs at $\lesssim 1/3$ the maximum intensity.) Thus, the difference between the extrapolated onset and the rotationally adiabatic value is ~ 0.005 eV for CH$_4$, and ~ 0.004 eV for CH$_4$. 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 CH$_4$ and CD$_4$, 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–Condon factor for the first vibrational step in the transition CD$_4 \rightarrow$ CD$_4^+$ is weaker than the corresponding one in CH$_4$. 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; $0.178^2 \pm 0.008$, $0.16^3 \pm 0.02$, and 0.08^8 eV.

The photoelectron spectrum of the first band in CH$_4$ (CD$_4$) 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 CH$_4$ and CD$_4$, the splitting of Jahn–Teller states is smaller in CD$_4^+$ (0.7 eV) than in CH$_4^+$ (0.8 eV). Also, the half-width of the entire band is distinctly narrower in CD$_4^+$, the ratio of bandwidths being about 1.18.

The vibrations in CH$_4$ are essentially hydrogenic motions. A comparison of the vibrational frequencies of CH$_4$ and CD$_4$ shows that they differ by a factor of approximately $\sqrt{2}$. It can readily be shown that the classical amplitudes of vibration in the $v'' = 0$ states then differ by $\sim \sqrt[4]{2} = 1.189$.

The classical turning points roughly define the Franck–Condon width, which should therefore be correspondingly narrower in CD$_4$. Since one is starting out with a more localized wave function, the Franck–Condon overlap with the adiabatic geometry of the ion is much weaker for CD$_4^+$, and hence it is more difficult to measure.

[1] See, for example, C. A. Coulson and H. L. Strauss, Proc. R. Soc. London Ser. A **269**, 443 (1962); R. N. Dixon, Mol. Phys. **20**, 113 (1971); W. Meyer, J. Chem. Phys. **58**, 1017 (1973); D. Feller and E. R. Davidson, *ibid.* **80**, 1006 (1983); M. N. Paddon-Row, D. J. Fox, J. A. Pople, K. N. Houk, and D. W. Pratt, J. Am. Chem. Soc. **107**, 7696 (1985).

[2] A. J. C. Nicholson, J. Chem. Phys. **43**, 1171 (1965).

[3] V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harlee, J. Chem. Phys. **42**, 3791 (1965).

[4] B. Brehm, Z. Naturforsch. Teil A **21**, 196 (1966).

[5] W. A. Chupka and J. Berkowitz, J. Chem. Phys. **54**, 4256 (1971).

[6] A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, Int. J. Mass Spectrom. Ion Phys. **1**, 285 (1968).

[7] B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, J. Chem. Phys. **53**, 768 (1970).

[8] C. R. Brundle, M. B. Robin, and H. Basch, J. Chem. Phys. **53**, 2196 (1970).

[9] J. W. Rabalais, T. Bergmark, L. O. Werme, L. Karlsson, and K. Siagbahn, Phys. Scr. **3**, 13 (1971).

[10] A. W. Potts and W. C. Price, Proc. R. Soc. London Ser. A **326**, 165 (1972).

[11] (a) G. Herzberg, *Molecular Spectra and Molecular Structure. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1945), Vol. 2; (b) K. S. Krasnov, *Molekulyarnie Postoyannie Neorganicheskikh Soedinenii* (Khimiya, Leningrad, 1979).

[12] The calculated frequencies of CH$_4$ 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 CD$_4$, CH$_4^+$, and CD$_4^+$ have been made available to us by Dr. L. A. Curtiss, Chemical Technology Division, Argonne National Laboratory.

[13] J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. Defrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, Int. J. Quantum Chem. Symp. **15**, 269 (1981).

[14] J. Berkowitz, *Photoabsorption, Photoionization and Photoelectron Spectroscopy* (Academic, New York, 1979).

[15] G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, Princeton, 1966).