

Measurements of Threshold Electrons in the Photoionization of Methane*

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Despite recent advances in the accurate experimental determination of molecular ionization energies, there is considerable variation in the reported values of the ionization potential of methane.¹ Measurement of the total ionization by photon impact led Watanabe to $I(\text{CH}_4) = 12.99 \pm 0.01$ eV,² a value supported by subsequent investigation.³ However, Dibeler *et al.* employing mass analysis of the positive ion current, found that a weak CH_4^+ current could be detected with an apparent onset at a photon energy of only 12.71 eV.⁴ This same appearance potential was independently determined by Nicholson observing the total ionization under photon impact.⁵

Recently, Brehm,⁶ and subsequently, Chupka,⁷ using mass analysis to study positive ions, have found evidence of a CH_4^+ current at photon energies as low as 12.55 eV. By way of contrast with the trend of the work indicated above, recent experiments using photoelectron spectroscopy support Watanabe's first reported value for $I(\text{CH}_4)$. Thus, Al-Joboury and Turner, ob-

serving only photoelectrons produced by 584-Å radiation, claim an ionization potential of CH_4 at 12.99 eV.⁸ Also, Hamrin *et al.*, who used a similar photoelectron approach, reported a higher ionization potential at 23.1 eV and, in addition, indicated that their work supported a first ionization potential at 13.0 eV.⁹

It would appear that photoelectron spectroscopy tends to favor a value that differs somewhat from the results recently obtained in other kinds of photoionization experiments. It is the purpose of this Note to report photoelectron measurements in CH_4 which are in better agreement with these other types of photoionization studies.

The experimental technique, which involves measurements of threshold energy electrons as a continuous function of the incident photon energy, has been described elsewhere.¹⁰ Briefly, photoelectrons are accelerated and then analyzed by a 127° cylindrical electrostatic energy analyzer. The analyzer energy is chosen to equal the acceleration energy, in this case 6 eV. Since all electrical potentials are fixed and only the incident photon energy is varied, it is believed that the electron collection efficiency is constant. The photoelectron count rate divided by incident photon flux, as observed in CH_4 , is shown in Fig. 1. Both the monochromator bandwidth of 2.5 Å and the electron energy analyzer bandwidth of about 0.13 eV (at the

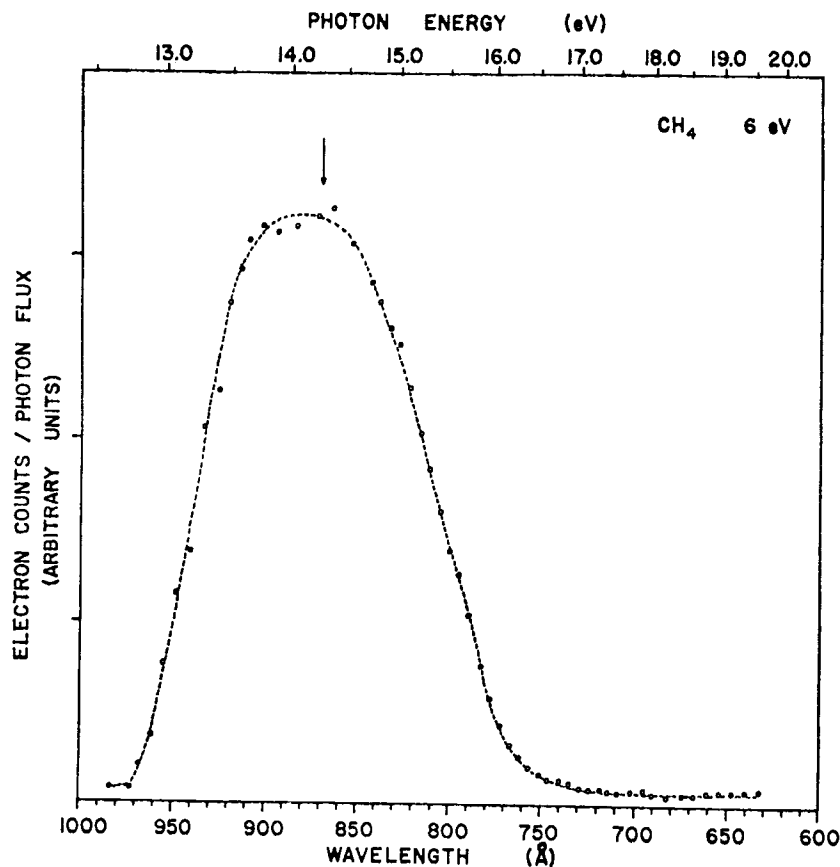


FIG. 1. Photoelectron count rate divided by photon flux as a function of wavelength of the primary photon. A nominal 6-eV analysis energy (see text) was used. The arrow locates the energy corresponding to dissociative ionization.

nominal 6-eV analysis energy) are substantially smaller than the half-width of the envelope of the observed spectrum. The apparent onset at 12.75 ± 0.05 eV is in much better agreement with the photoionization studies of positive ions⁴⁻⁷ than with the previous photoelectron studies.^{8,9} In the energy region from threshold up to about 14.5 eV there is evidence of structure in the curve. However, at the resolution employed these features remain unresolved. The energy coordinate corresponding to the threshold for the production of fragment ions⁷ is indicated by a solid arrow in Fig. 1. It is evident that the envelope of transition probabilities corresponding to the production of vibrationally excited CH_4^+ is continuous with the transition probability for the production of fragment ions. Also, the maximum of the transition probability very nearly coincides with the energy coordinate of the onset of the dissociative process, providing further support for the previously suggested view that ionization of CH_4 involves a large change of the molecular geometry.⁴ It is important to realize that this interpretation implies the possibility that the energy of onset of ionization found in the present study may not correspond to the adiabatic ionization potential but rather represents an upper bound on this quantity.

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