Evidence of rotational autoionization in the threshold region of the photoionization spectrum of CH$_3$

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The photoionization spectrum of the threshold region of CH$_3$ equilibrated at room temperature has been recorded and compared to the zero electron kinetic energy (ZEKE) spectrum of Blush et al. [J. Chem. Phys. 98, 3557 (1993)]. The ionization onset region is at $\sim$70 cm$^{-1}$ higher energy than previous high-temperature photoionization work [Chupka and Lifshitz, J. Chem. Phys. 48, 1109 (1967)], but still $\sim$34 cm$^{-1}$ lower than that implied by invoking only direct ionization. The residual discrepancy can be accounted for by including fully allowed quadrupole-induced and partially allowed dipole-induced rotational autoionization, thus making the observed onset completely congruous with the ZEKE ionization potential. In addition, the fragment appearance potential of CH$_3^+$ from CH$_4$ was redetermined by accurate fitting as $AP_{CH_3^+}/CH_4=14.322\pm0.003$ eV. With the very precise ZEKE ionization potential, this yields the best current value for the bond dissociation energy in methane, $D_0$(H–CH$_3$)$=4.848\pm0.003$ eV $=103.40\pm0.07$ kcal/mol (104.96$\pm0.07$ kcal/mol at 298 K). © 1997 American Institute of Physics. [S0021-9606(97)03247-9]

I. INTRODUCTION

The methyl radical, produced by pyrolysis of suitable precursors, was examined previously$^1$ by photoionization at a resolution of $\sim$100 cm$^{-1}$. The threshold region is dominated by a strong 0$\rightarrow$0 vibrational Franck–Condon factor, manifesting itself as a “sharp” step with a half-rise at 9.825$\pm0.010$ eV. Normally, this value would be interpreted as the adiabatic ionization potential (IP). However, it was $\sim$150 cm$^{-1}$ lower than Herzberg’s spectroscopic determination$^2$ of 79.392$\pm5$ cm$^{-1}$=9.8434$\pm0.0006$ eV, obtained by extrapolating early members of three Rydberg series. Although the general appearance of the photoionization threshold led them to the assumption that autoionization does not occur in the threshold region, Chupka and Lifshitz$^3$ concluded that the discrepancy must nevertheless be due to an inadequate interpretation of the threshold shape.

Subsequent photoelectron spectroscopic (PES) investigations$^4$ at a resolution of $\sim$120–160 cm$^{-1}$ yielded$^4$ 9.837$\pm0.005$ eV as the adiabatic IP, in reasonable agreement with Herzberg’s value.$^2$ More recently,$^6$ the ionization threshold region of CH$_3$ (produced by flash pyrolysis of azomethane) was examined by pulsed field ionization (PFI). The rotationally resolved (\~1.5 cm$^{-1}$) spectrum of near-zero kinetic energy electrons (ZEKE) yielded an adiabatic IP of 79.349$\pm3$ cm$^{-1}$=9.8380$\pm0.0004$ eV, somewhat (43 cm$^{-1}$) lower than Herzberg’s value$^2$ (and in excellent agreement with the coarser PES value$^3$), but still 105 cm$^{-1}$ higher than the photoionization value.$^1$

If direct ionization were indeed the only significant contributor to the ionization threshold region of CH$_3$, then an integral over the PES or ZEKE spectrum should fairly reproduce the threshold shape of the photoionization yield curve. A brief glance at the ZEKE spectrum$^6$ suggests that such an integral would tend to produce a relatively simple steplike shape, with the midrise not too far from the position of the head of the $Q$ branch. The hot rotational distribution of CH$_3$ (1000–1300 K) in the photoionization experiment$^1$ is expected to extend the breadth of the branches and thus decrease the slope of the threshold, but should not cause an appreciable net shift to lower energy. Hence, in the absence of autoionization, there appears to be no obvious reason why the midrise of the photoionization step should not yield an IP compatible with PES or PFI.

In this paper we would like to show that the photoionization spectrum of the threshold region of CH$_3$, when equilibrated at room temperature, yields an ionization onset closer to the ZEKE value$^6$ than previous high-temperature photoionization experiments,$^1$ and demonstrate that the apparent residual discrepancy can be explained by invoking rotational autoionization.

II. EXPERIMENT

The basic instrumentation employed here was recently described elsewhere.$^7$ CH$_3$ was produced in situ by hydrogen abstraction from methane. Fluorine atoms were generated in a low-pressure microwave discharge through pure fluorine and piped into a small cuplike region, where they reacted with the methane precursor. The construction of the radical source ensures that species emanating into the ionization region have undergone several collisions with the source walls and are thus equilibrated to ambient temperature. The reaction yield was optimized by manually adjusting the output power of the microwave source and the flows of F$_2$ and CH$_4$. The experiments utilized the many-lined Werner and Lyman emission bands of H$_2$, which provided an accurate internal wavelength calibration.
III. RESULTS

Figure 1 displays a mass-resolved (m/e = 15) scan of the threshold region of CH$_3$ covering 125–128 nm, recorded at medium resolution (~50 cm$^{-1}$), and at 0.02 nm point density. The wavelength scale calibration is believed to be correct to <0.01 nm (~5 cm$^{-1}$). The overall shape of the threshold, which corresponds to the vibrationless (0→0) CH$_3$ $^{3}$P$_1$ ←CH$_3$, $^{3}$D$_2$ $^{3}$A$_{2}$ transition, is indeed that of a giant step. The nominal midrise position is at ~126.08±0.02 nm=9.8338±0.0016 eV, some 70 cm$^{-1}$ higher than the value reported by Chupka and Lifshitz, but still ~34 cm$^{-1}$ shy of the PFI value. The plateau region displays muddled autoionization structure converging to higher vibrational levels of the ion, while the ascending portion of the step shows some substructure in the form of gentle steps or undulations. The very weak steplike structure at ~127.02±0.05 nm is readily assigned as a $\nu_2$ hot band ($a''_u$ out-of-plane bend, 8–10 606.5 cm$^{-1}$). Its intensity (~1%) roughly corresponds to room temperature Boltzmann population of $\nu_2$ (~5%), reduced by the 0→1 Franck–Condon factor. The stronger 1→1 transition falls ~780 cm$^{-1}$ beyond the threshold. The remaining humplike undulations observable in the threshold region (peaking at ~126.5, ~126.2, and perhaps ~125.9–126.0 nm) are difficult to rationalize via vibrational hot bands.

IV. DISCUSSION

A. Direct ionization in the threshold region

Using known rotational constants of CH$_3$ and CH$_3^+$, we have produced a simple simulation of the relevant rotational structure. The continua accessible from the ground state of CH$_3$, $^{3}$P$_1$ $^{3}$A$_2$, consist of the CH$_3^+$ $^{3}$P$_1$ $^{3}$A$_2$ ion core coupled to $ksa'_1$, $kda'_1$, and $kde''$ outgoing electron channels. These mirror the Rydberg series (β, δ, and γ) observed by Herzberg. The $ksa'_1$, β $^{3}$A$_1$; and $kda'_1$, δ $^{3}$A$_1$; continua are accessible by parallel, and $kde''$, γ $^{3}$E$^+$ by perpendicular transitions. The $\Delta J=0$, ±1 selection rule leads to $\Delta N=0$, ±1, ±2 (ΔK = 0) for parallel and $\Delta N=0$, ±1, ±2, ±3 (ΔK = 0, ±2), as shown by Blush et al. for perpendicular transitions. As manifested by the ZEKE spectrum, propensity rules tend to emphasize $\Delta N=0$, ±1 transitions. Thus, the simulation uses only P, Q, and R branches, with the addition of a weak O branch. However, it includes both $\Delta K = 0$ and $\Delta K = ±2$ subbands, in spite of the fact that Blush et al. state that there is very little indication of the latter. Apparent evidence to the contrary is the line assigned as $R_0$. With only $\Delta K = 0$ available, it would require $N^+ = 1$, $K^+ = 0$ as the final level, nonexistent by virtue of nuclear spin statistics if CH$_3^+$ is of $D_{5h}$ symmetry. With $\Delta K = ±2$, there are several small lines in the immediate vicinity, accounting for the experimental observation.

The individual line intensities were estimated by taking into account the nuclear spin statistics, degeneracy, and the Boltzmann population of the initial states, as well as the nuclear spin statistics and degeneracy of the ionic states. To simulate the direct ionization portion of the photoionization threshold, the calculated transitions were convoluted with the experimental resolution and integrated. A baseline offset to accommodate the $\nu_2$ hot band was added, and the intensity adjusted to match the relative experimental scale, making some allowance for the autoionization structure in the plateau region. The result is shown in Fig. 2(a), as a thin solid line on an energy scale relative to the ionization potential of Blush et al. (79349±3 cm$^{-1}$). The direct ionization model clearly predicts that the adiabatic IP is near the midrise point. Compared to the experiment, the curve is shifted nonuniformly to higher energy. Thus, one concludes that direct ionization alone is not sufficient to explain the photoionization threshold.

B. Autoionization in the threshold region

The modeling of autoionization phenomena is more intricate. The β, δ, and γ Rydberg states converging to every
rotational level of the ion can autoionize if the appropriate (i.e., the same symmetry, parity, and total angular momentum) continuum and mechanism is available. Since CH$_3^+$ does not have a permanent dipole moment, only quadrupole ($\Delta N^+ = \text{even}$) autoionization will be fully allowed. While the nsa$^*_1 \beta^2 A'_1$ and nda$^*_1 \delta^2 A'_1$ Rydberg states are not capable of autoionizing via this mechanism, the nde$^*_n \gamma^2 E''$ Rydberg states have two $J$ values in common with the kde$^*_n$ continuum built upon the $N^+\cdot-2$ level. The partial cross section associated with these Rydberg states will appear as an autoionizing quasicontinuum, producing a miniature steplike contribution to the ion yield with an onset at the $N^+\cdot-2$ level of the ion. Without autoionization, the corresponding contribution would have had an onset at $N^+$ level. The simulation that includes autoionization from the appropriate $J$ space of nde$^*_n \gamma^2 E''$ Rydberg states is depicted in Fig. 2(b) (the thick solid line). The curve grazes the experimental points from the high-energy side and appears to account for the bulk of the observed threshold shape, missing only the additional intensity present in the regions of the three humps mentioned in Sec. III. Rather than at the midrise, the adiabatic IP is now located closer to the upper end of the step.

The nsa$^*_1 \beta^2 A'_1$ and nda$^*_1 \delta^2 A'_1$ Rydberg states have one $J$ value in common with both the ksa$^*_1$ and kda$^*_1$ continuum channels built upon the $N^+-1$ level of the ion, while the nde$^*_n \gamma^2 E''$ Rydberg states have three $J$ values in common with the analogous kde$^*_n$ continuum. In addition, the $\gamma$ Rydberg states also have one $J$ value in common with the kde$^*_n$ continuum built upon the $N^+\cdot-3$ level of the ion. Thus, if a dipole mechanism were available, one-half of the $J$ space of $\beta$ and $\delta$ Rydberg states and three-quarters of the $J$ space of $\gamma$ Rydberg states with appropriate $n^*$ values could autoionize. If fully allowed, such autoionization could make the $S$ (and $T$) rotational branches unavailable to ZEKE-type experiments, which rely on time-delayed pulsed-field ionization of very high $n^*$ Rydberg states. However, in the $O$, $P$, $Q$, and $R$ branches there is a significant number of $J$ values for which autoionization is not possible. These nonautoionizing states are sufficient to comfortably reproduce the line positions and approximately the intensities measured by Blush et al.\textsuperscript{6}

The assumption that the dipole mechanism is fully operating produces the simulation depicted in Fig. 2(c) (dashed line). Not surprisingly, this curve overestimates the ion yield, grazing the data on the low-energy side. The experimental trace could now be perceived as if it consisted of curve (c) with the addition of broad valleys, shown inverted by subtracting the experimental data from curve (c), Fig. 2(d). One valley is centered at $-210 \text{ cm}^{-1}$, with perhaps two additional poorly resolved valleys at $-90$ and $0 \text{ cm}^{-1}$. The structure is obscured at the high-energy side partly by the (vibrational) autoionization occurring in the plateau region in the experiment, and partly by the fact that the $R$ branch is slightly overemphasized in the simulation. The position of the valleys coarsely resembles an unresolved rotational spectrum shifted to lower energy by $-90$–$120 \text{ cm}^{-1}$.

One potentially active dipole mechanism can be traced to the dipole induced by the repeller field, which is always present in photoionization mass spectrometric experiments. In this case one would expect to see a dependence on the magnitude of the repeller field. To explore this aspect, we have recorded spectra at various repeller settings, ranging from 0.8 to 12.5 V/cm. Within the statistical uncertainty of the data, all spectra appeared identical. Another possible candidate is the momentary dipole that occurs as CH$_3^+$ undergoes the zero-point out-of-plane vibrational motion. This dipole will not be very efficient in inducing autoionization, since, in classical terms, its vibrational period is about three orders of magnitude shorter than the orbital period of an $n^* \approx 50$ Rydberg electron. On the other hand, its efficiency has to be compared to the lifetime of the Rydberg states in the absence of autoionization, which can be substantial. However marginal, such a mechanism will be more efficient for low Rydberg states (with shorter orbital periods), and will become less effective as $n^*$ increases. This $n^*$ dependence will change the shape of the contribution to the ion yield. Instead of a flattop step, the contribution will now display an onset corresponding to lower $n^*$ states, followed by a depression and regaining intensity close to the ionization limit. The depression corresponds to the Rydberg states with intermediate $n^*$ values, for which this mechanism is inefficient. Very high $n^*$ states, close to the ionization limit, can autoionize via an induced dipole mechanism even in weak fields, since their polarizability increases as $n^*$. A similar overall effect, albeit related to induced-dipole autoionization, has been postulated previously for N$_2$.\textsuperscript{13} The anticipated cumulative effect of such depressions in the partial ionization cross sections is to create broader spectral valleys preceding the onsets of the principal rotational branches.

The modeling of partially allowed dipole-induced autoionization, whether by a mechanism similar to the one described above or some other, would be a tall task even with the aid of sophisticated quantum mechanical calculations capable of yielding the proper $n^*$ dependence of autoionization probability. However, in order to qualitatively test the plausibility of the ideas outlined above, we have performed exploratory simulations which incorporated quenching of dipole-allowed autoionization for intermediate $n^*$ values in a very crude manner. These tests suggested that such quenching effects could indeed lead to a structured threshold shape with broad valleys roughly in the appropriate positions.

Overall, the simulations shown in Fig. 2 demonstrate that the bulk of the photoionization threshold shape can be explained by direct ionization via a weak $O$ branch and normally developed $P$, $Q$, and $R$ branches, combined with quadrupole-induced autoionization of nde$^*_n \gamma^2 E''$ Rydberg states. The additional structure in the experimental spectrum is probably caused by partially allowed dipole-induced ionization of all three (nsa$^*_1 \beta^2 A'_1$, nda$^*_1 \delta^2 A'_1$, and nde$^*_n \gamma^2 E''$) Rydberg series converging to the threshold. The implication of the autoionization model is that the selection of the midrise of the threshold step as adiabatic IP is not appropriate in this case. Instead, the proper value is close to the high end of the step. However, the traditional shortcut, which selects the midrise of the threshold step as the adiabatic IP (and thus effectively ignores rotational substructure
even if only direct ionization were present), would in practice lead to a relatively small error (for thermodynamic purposes) of 0.0042 eV=34 cm\(^{-1}\)=0.10 kcal/mol.

The described threshold effects involving autoionization are ultimately thermal in their nature, inasmuch as their intensity is derived from the Boltzmann population of rotational levels of the initial neutral species. As mentioned in Sec. I, if only direct ionization were present, the enhanced temperatures would simply extend the breadth of the branches and thus decrease the slope of the threshold, without causing an appreciable net shift of the midrise to lower energy. However, rotational autoionization builds up intensity below the nominal threshold(s). While the magnitude of the resulting departure from the simple midrise interpretation is small to moderate at room temperature, it is expected to be substantially larger at elevated temperatures, such as used previously.1

With the autoionization model proposed here, the room-temperature photoionization experiment becomes completely compatible with the precise adiabatic IP value of 9.8380 ±0.0004 eV obtained by Blush et al.5 If, instead, the spectroscopic value\(^6\) of 9.8434 ±0.0006 eV is used in the modeling, a much poorer fit to the data is obtained. Compared to Fig. 2, the simulated curves appear shifted to higher energy to the extent that even the full inclusion of dipole-induced autoionization still substantially underestimates the experimental data, clearly indicating that this IP value is too high.

C. Thermodynamical consequences

Herzberg’s extrapolated value\(^2\) for IP(CH\(_3\)) quoted\(^14\) as 9.843±0.002 eV, and a photoionization measurement\(^15\) of the appearance potential (AP) of the CH\(_3\)\(^+\) fragment from CH\(_4\), AP\(_0\)(CH\(_3\)\(^+\)/CH\(_4\))=14.320±0.004 eV, which lead to \(D_0(\text{H–CH}_3)=103.2±0.1\) kcal/mol, are the basis for the recently recommended\(^14\) values \(D_0(\text{H–CH}_3)=103.3±0.1\) kcal/mol and \(\Delta H_f^{298}(\text{CH}_3)=35.0±0.1\) kcal/mol. Using the PFI value\(^6\) for IP(CH\(_3\)) instead of Herzberg’s, introduces a slight variance of ~0.12 kcal/mol. However, most of this shift (~0.09 kcal/mol) can be compensated for by using the alternate determination of AP\(_0\)(CH\(_3\)\(^+\)/CH\(_2\))=14.324±0.003 eV by McCulloh and Dibeler,\(^16\) which appears to be at least as reliable as Chupka’s.\(^15\) In view of the two slightly different determinations of AP(CH\(_3\)\(^+\)/CH\(_4\)), we have decided to reexamine the fragment yield curve of CH\(_3\)\(^+\) from CH\(_4\) and use our recently developed fitting procedures\(^5,17\) to either confirm or amend the appearance potential. A full account of the fitting procedure used here has been given recently elsewhere.\(^7\) Figure 3 shows the experimental data recorded at 300 K and the fit, barely discernible from the points, as well as the implied ion yield curve corresponding to 0 K. The derived AP at 0 K is 14.322±0.003 eV, in very good agreement (within the respective error bars) with both previous determinations,\(^15,16\) and, in fact, it coincides with their arithmetic average.

With the PFI-ZEKE value IP(CH\(_3\))=9.8380 ±0.0004 eV, which appears to be fully supported by the present study, our redetermined AP\(_0\)(CH\(_3\)\(^+\)/CH\(_4\))=14.322±0.003 eV yields the best current value for the bond dissociation energy in methane of \(D_0(\text{H–CH}_3)=4.484±0.003\) eV=103.40±0.07 kcal/mol (104.96±0.07 kcal/mol at 298 K), only a shade higher than the most recent recommendation.\(^14\) With auxiliary heats of formation,\(^18\) this translates into \(\Delta H_f^{298}(\text{CH}_3)=35.84±0.09\) kcal/mol and \(\Delta H_f^{298}(\text{CH}_3)=35.0±0.09\) kcal/mol. The corresponding heat of formation of the CH\(_3\)\(^+\) ion is \(\Delta H_f^{298}(\text{CH}_3)=262.7±0.09\) kcal/mol.

V. CONCLUSION

Earlier photoionization work\(^1\) on the methyl radical, which was generated by pyrolysis of dimethyl mercury and/or methyl nitrate at 1000–1300 K, implies an adiabatic IP that is lower than the PFI-ZEKE determination\(^6\) by 105 cm\(^{-1}\). When CH\(_3\) is equilibrated at room temperature, the ionization onset region appears ~70 cm\(^{-1}\) closer to the PFI-ZEKE value. However, a simple interpretation of the threshold shape that includes only direct ionization, still produces an apparent discrepancy of ~34 cm\(^{-1}\). The residual disparity can be accounted for by including fully allowed quadrupole-induced and partially allowed dipole-induced rotational autoionization. This makes the observed photoionization onset completely congruous with the ZEKE ionization potential\(^6\) of 9.8380±0.0004 eV, and indicates that Herzberg’s extrapolated value\(^2\) of 9.8434±0.0006 eV is slightly too high. The autoionization model also helps rationalize why the ionization onset of thermally hot CH\(_3\) appears to be depressed when compared to other data.

In addition, the fragment appearance potential of CH\(_3\)\(^+\) from CH\(_4\) was redetermined by accurate fitting as AP\(_0\)(CH\(_3\)\(^+\)/CH\(_4\))=14.322±0.003 eV. With the very precise ZEKE ionization potential, this yields the best current value for the bond dissociation energy in methane, \(D_0(\text{H–CH}_3)=4.484±0.003\) eV=103.40±0.07 kcal/mol (104.96±0.07 kcal/mol at 298 K).
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