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Rotationally resolved threshold photoelectron spectrum of the methyl radical

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We report the rotationally resolved, one-photon threshold photoelectron spectrum of the methyl radical, CH_3, produced by supersonic-jet, flash pyrolysis. Only rotational transitions with $\Delta K = 0, \pm 2$ are observed and this result is shown to be consistent with photoionization selection rules in D_{3h} symmetry. Assignment of the threshold photoelectron spectrum results in an adiabatic ionization potential of $79\,349 \pm 3$ cm^{-1}.

We report the rotationally resolved threshold photoelectron spectrum of the methyl radical, CH_3, in a pulsed supersonic jet, obtained by the pulsed field ionization (PFI) technique using coherent vacuum ultraviolet (vuv) radiation. The spectrum contributes to the limited body of high-resolution (1.5 cm^{-1} in this case) photoionization studies of radicals,[1-3] and represents the first polyatomic radical to be rotationally resolved. The observed cation rotational distribution provides interesting insights into the photoionization selection rules of a symmetric top molecule. The experiment also demonstrates the utility of using high-resolution photoelectron spectroscopy in studying the structure and thermochemistry of hydrocarbon radicals, and the corresponding carbonium ions.

The radical source,[4,5] the coherent vuv radiation source[6] and the photoelectron spectrometer[7] have all been previously described. Methyl radicals are produced by supersonic-jet flash pyrolysis (1300 K/10 μs) of a 2% mixture of azomethane, CH_3NNCH_3, in argon at a stagnation pressure of 900 Torr. Tunable vuv radiation near the methyl ionization potential (~ 126 nm) is produced by resonant difference frequency mixing in krypton[8,9] via the $5p[2\frac{1}{2}]_2 \leftarrow \leftarrow 4p$ two-photon transition ($2\omega_1 - \omega_2$, $\omega_1 = 216.67$ nm, $\omega_2 \sim 770$ nm). Two separate Nd:YAG-pumped dye laser systems are used to produce radiation at ω_1 and ω_2; ω_1 is generated via sum frequency mixing of the visible and second harmonic outputs of one dye laser using DCM dye and ω_2 is generated in the second dye laser employing LDS 765 dye. The two laser pulse trains (20 Hz) are synchronized by external timing to within ± 1 ns and focused with an achromatic lens (100 mm f.l.) into a pulsed, free-jet expansion of krypton. The vuv difference frequency, unconverted ω_1 and ω_2, as well as the vuv sum frequency ($2\omega_1 + \omega_2$) beams are captured by a Pyrex capillary wave guide that delivers the radiation to the interaction region of the photoelectron spectrometer. A small flow of xenon gas (0.5 Torr) is added to the center of the capillary to absorb the sum frequency. High-resolution threshold photoelectron spectra are obtained by the pulsed field ionization (PFI) variant of zero-kinetic-energy (ZEKE) photoelectron spectroscopy.[1,10] In the present experiment, a dc field of 0.1 V/cm in the interaction region removes direct photoelectrons during a 600 ns delay, after which a -0.8 V/cm pulse ionizes any population of high-n ($\geqslant 150$) Rydberg states which lie within 2 cm^{-1} of a cationic rotational level. The resulting pulse of delayed electrons is measured as a function of the wavelength to comprise the threshold photoelectron spectrum.

The rotationally resolved one-photon PFI spectrum for the methyl radical is shown in the upper panel of Fig. 1. The rotational structure is quite similar to that observed for the bound–bound β, $\delta \leftarrow X$ bands in CH_3 and CD_3 which are parallel electronic transitions ($\Delta K = 0$) with simple P, Q, and R branches reminiscent of a diatomic molecule.[11] Due to the similarity of the ground and excited state structures, each branch line is comprised of many closely spaced $\Delta K = 0$ subband lines.[11,12] The PFI spectrum shows little or no evidence of the more diffuse structure expected for perpendicular transitions with $\Delta K = \pm 1$ subbands. For photoionization, we define $\Delta K = K^+ - K''$ and $\Delta N = N^+ - N''$, where the plus superscript refers to the cation and the double prime superscript refers to the ground state of the radical. The total angular momentum apart from spin, N, is used instead of J to avoid unnecessary complications involving the change in multiplicity. Using the highly accurate rotational constants reported by Yamada *et al.*[13] for the $^2A_2''$ neutral ground state and by Crofton *et al.*[14] for the $^1A_1'$ ground state of the cation, the sharp structure in the PFI spectrum can be assigned to prominent P, Q, and R branches with a few lines belonging to the O branch with $N'' \geqslant 5$. The surprisingly intense $O(6)$ line is attributed to near resonant autoionization which is known to result in perturbed intensities, particularly for branches with $\Delta J(N) \leqslant 0$, in the PFI-ZEKE spectra of other molecules.[15-17] The rotational constants are also used to generate the spectral simulation shown in the lower panel of Fig. 1. Only $\Delta K = 0$ transitions are included in the simulation and line intensities are based solely on the ground state rotational temperature and the 2:1 *ortho* to *para* nuclear spin state ratio required for CH_3.[11,14] The latter is responsible for much of the intensity modulation in the P and R branches at low N''. The rotational temperature of 250 K is only approximate, but is reasonably based on an earlier resonant multiphoton ionization (MPI) mea-
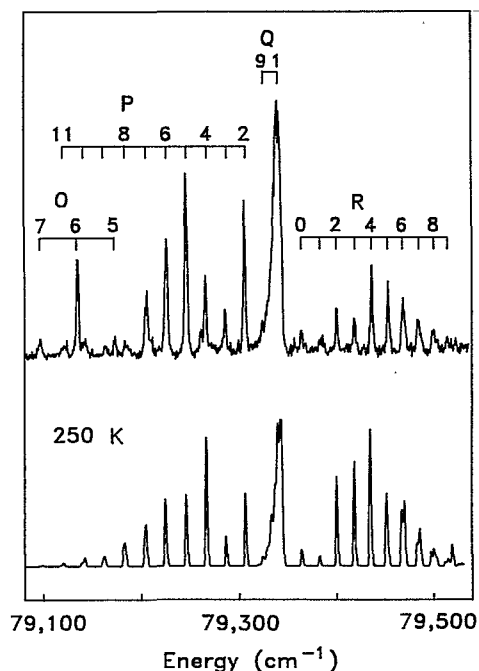
FIG. 1. Rotationally resolved threshold photoelectron spectrum for the one-photon ionization transition CH_3^+ ($^1A_1'$, N^+) $+e^-$ $\leftarrow CH_3$ ($^2A_2''$, N''). The rotational branch labels refer to $\Delta N = N^+ - N''$ where the branch ladders are numbered by N''. Upper curve: experimental pulsed field ionization (PFI) spectrum. Lower curve: calculated threshold photoelectron spectrum consisting of $\Delta K = 0$ transitions only and using a ground state rotational temperature of 250 K. The relative intensities reflect the populations of the ground state rotational levels and do not include line strength factors.

surement of allyl radical produced by the flash pyrolysis source.[18] Extraction of the band origin by rotational analysis, and correction for the field-induced shift of the observed peaks, yields an adiabatic ionization potential for CH_3 of $T_0 = 79\ 349 \pm 3$ cm^{-1}, or 9.8381 ± 0.0004 eV. This value is in reasonable agreement with that obtained by conventional photoelectron spectroscopy,[19] but lies 44 cm^{-1} below Herzberg's value determined by extrapolation of the nda_1' Rydberg states with relatively low principal quantum numbers ($n = 3$–8).[11]

The methyl radical and cation are oblate symmetric tops, belonging to the D_{3h} molecular point group. Dipole-allowed transitions from the $\tilde{X}\ ^2A_2''$ ground state of CH_3 occur to final states [ion core ($^1A_1'$) + photoelectron] with an overall symmetry (ignoring spin) of A_1' for parallel transitions and E'' for perpendicular transitions. These correspond to allowed photoelectron continuum channels with ksa_1', kda_1', and kde'' symmetry, respectively. Transitions to p-type ($l = 1$) continua, which transform as a_2'' and e', are dipole forbidden. The allowed final states are consistent with atomic selection rules ($\Delta l = \pm 1$) as would be expected given the atomic character of the outer a_2'' molecular orbital, which is essentially an out-of-plane $2p$ orbital localized on the central carbon atom. Molecular symmetry considerations allow for transitions to the kfa_1' and kfe'' continua, but a further theoretical analysis would be required to determine the strength of these transitions that

are forbidden in the united atom limit.[11] Herzberg reports the observation of low-n Rydberg states in the absorption spectrum of methyl radical which he assigns to three series corresponding to nsa_1' (β bands), nda_1' (δ bands) and nde'' (γ bands).[11] Due to predissociation, perpendicular transitions to the nde'' states are too diffuse to rotationally resolve, whereas excitations to the nsa_1' Rydberg states exhibit distinct rotational structure characteristic of parallel transitions. Integrated oscillator strength measurements for the $n = 3$ Rydberg levels indicate that the E'' perpendicular transition is significantly stronger than the corresponding A_1' parallel transitions.[20]

Our observation of only $\Delta K = 0$ transitions for photoionization of CH_3 suggests that the ka_1' continua dominate at threshold, in apparent disagreement with the spectroscopic measurements discussed above. Alternatively, the very high-n, nde'' Rydberg states may be rapidly predissociated, as they are at low n,[11] and consequently not detectable in the PFI measurement which employs a 600 ns delay between excitation and field ionization. Neither explanation seems likely in light of previous PFI measurements on small polyatomic molecules, e.g., $H_2O^{21,22}$ and NH_3,[23] which exhibit rotational transitions associated with all allowed photoelectron continua and no clear evidence for rapid nonradiative decay processes, such as predissociation, which result in depopulation of very high-n Rydberg states ($n \geqslant 150$). A closer analysis of the photoionization selection rules, following work done by Lee et al. on H_2O,[22] gives the selection rule $\Delta K = \mu + \lambda$, where μ and λ are the molecular frame projections of the photon polarization and the photoelectron orbital angular momentum, respectively. Values for μ and λ can be obtained by direct inspection of the D_{3h} character table. For parallel transitions to ka_1', one obtains $\mu = \lambda = 0$, and for perpendicular transitions to ke'' one obtains $\mu = \lambda = \pm 1$. This yields the surprising result, contrary to the bound–bound selection rule, that for both parallel and perpendicular transitions ΔK is even, and odd ΔK transitions are forbidden. The methyl PFI spectrum is completely consistent with this prediction and it is not necessary to require the dipole-allowed ke'' continuum to be weak or undetectable.

The above symmetry analysis shows that transitions to ke'' continua ($\mu = \lambda = \pm 1$) can lead to $\Delta K = \pm 2$ as well as $\Delta K = 0$ subbands. As a result, it should be possible to confirm the presence of perpendicular final states through the observation of $\Delta K = \pm 2$ branch lines. Unfortunately, nuclear spin statistics eliminates 67% of the potential $\Delta K = \pm 2$ transitions, including the more thermally populated ortho ones. Consequently, it is difficult to assess the importance of $\Delta K = \pm 2$ transitions to the observed PFI spectrum. The noise level of the PFI spectrum prevents any conclusion other than the ke'' final states are not significantly more populated than the ka_1' final states. Accurate ab initio photoionization calculations such as those recently performed for H_2O^{22} will be required to go beyond the qualitative analysis of the CH_3 threshold photoionization spectrum presented in this work.

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[1] G. Reiser, W. Habenicht, K. Müller-Dethlefs, and E. W. Schlag, Chem. Phys. Lett. **152**, 119 (1988).

[2] G. C. Eiden, F. Weinhold, and J. C. Weisshaar, J. Chem. Phys. **95**, 8665 (1991).

[3] R. T. Wiedmann, R. G. Tonkyn, M. G. White, K. Wang, and V. McKoy, J. Chem. Phys. **97**, 768 (1992).

[4] J. A. Blush, H. Clauberg, D. W. Kohn, D. W. Minsek, X. Zhang, and P. Chen, Acc. Chem. Res. **25**, 385 (1992).

[5] D. W. Kohn, H. Clauberg, and P. Chen, Rev. Sci. Instrum. **63**, 4003 (1992).

[6] R. G. Tonkyn and M. G. White, Rev. Sci. Instrum. **60**, 1245 (1989).

[7] R. G. Tonkyn, J. W. Winniczek, and M. G. White, Chem. Phys. Lett. **164**, 137 (1989).

[8] R. Hilbig, G. Hilber, A. Lago, B. Wolff, and R. Wallenstein, in *Short Wavelength Coherent Radiation: Generation and Applications*, edited by R. G. Lerner (AIP, NY, 1986), p. 382.

[9] C. E. M. Strauss and D. J. Funk, Opt. Lett. **16**, 1192 (1991).

[10] K. Müller-Dethlefs and E. W. Schlag, Annu. Rev. Phys. Chem. **42**, 109 (1991).

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

[12] P. Chen, S. D. Colson, W. A. Chupka, and J. A. Berson, J. Phys. Chem. **90**, 2319 (1986).

[13] C. Yamada, E. Hirota, and K. Kawaguchi, J. Chem. Phys. **75**, 5256 (1981).

[14] M. W. Crofton, M. F. Jagod, B. D. Rehfuss, W. A. Kreiner, and T. Oka, J. Chem. Phys. **88**, 666 (1988).

[15] R. T. Wiedmann, E. R. Grant, R. G. Tonkyn, and M. G. White, J. Chem. Phys. **95**, 746 (1991).

[16] G. Reiser and K. Müller-Dethlefs, J. Phys. Chem. **96**, 9 (1992).

[17] R. G. Tonkyn, R. T. Wiedmann, and M. G. White, J. Chem. Phys. **96**, 3696 (1992).

[18] D. W. Minsek, J. A. Blush, and P. Chen, J. Phys. Chem. **96**, 2025 (1992); J. A. Blush, D. W. Minsek, and P. Chen, *ibid.* (in press).

[19] J. Dyke, N. Jonathan, E. Lee, and A. Morris, J. Chem. Soc. Faraday 2 **72**, 1385 (1976); T. Koenig, T. Balle, and W. Snell, J. Am. Chem. Soc. **97**, 662 (1975).

[20] M. J. Pilling, A. M. Bass, and W. Braun, Chem. Phys. Lett. **9**, 147 (1971).

[21] M.-T. Lee, K. Wang, V. McKoy, R. G. Tonkyn, R. T. Wiedmann, E. R. Grant, and M. G. White, J. Chem. Phys. **96**, 7848 (1992).

[22] M.-T. Lee, K. Wang, and V. McKoy, J. Chem. Phys. (submitted).

[23] W. Habenicht, G. Reiser, and K. Müller-Dethlefs, J. Chem. Phys. **95**, 4809 (1991).