

An electron-impact spectroscopy investigation of CH₃ and some of its pyrolytic precursors^{a)}

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The electronic spectrum of the methyl radical CH₃ was investigated by the technique of variable-angle electron energy-loss spectroscopy. By means of pyrolytic decomposition three possible sources of this radical were tried (tetramethyl tin, ethyl nitrite, and di-*t*-butyl-peroxide). The spectra of these precursors were obtained. Using di-*t*-butyl-peroxide, relative differential cross sections for the lowest allowed A_2'' $3s$ Rydberg transition in CH₃ (5.73 eV) were determined at incident energies of 50 and 25 eV. The behavior of the differential cross section for this band is analogous to that of a spin-allowed transition in a closed shell system and, as expected, in the vicinity of this band no transition of a spin-forbidden nature is detected.

I. INTRODUCTION

Free radicals play a major role in upper atmospheric chemistry, interstellar chemistry, and combustion chemistry. Many have low-lying electronic states energetically accessible under combustion conditions. In order to fully understand these processes it is necessary to understand the nature of the electronic states involved.

The methyl radical is one of the most important of the polyatomic free radicals and, being one of the simplest hydrocarbons, is a useful model system for molecular orbital theory. It has been extensively studied by Herzberg via optical techniques.¹ CH₃ is planar with D_{3h} symmetry and has the ground state electron configuration

$$(1a_1)^2(2a_1)^2(2e')^4(2a_2'')^1.$$

The ground state is of ${}^2A_2''$ symmetry, the unpaired electron lying in a p_z orbital of a_2'' symmetry. The lowest observed transition is the ${}^2A_1' \leftarrow {}^2A_2''3s$ Rydberg excitation at 5.73 eV. The forbidden excitation to the lowest ${}^2E'$ valence state has not been observed; however, calculations by Lengsfeld *et al.*² and McDiarmid³ place it about 1.5 eV above the lowest $3s$ Rydberg state. The transitions to the $3p$ Rydberg states are also dipole symmetry forbidden in D_{3h} symmetry but Hudgens *et al.*⁴ have found them to be at 7.42 eV by a resonantly enhanced multiphoton ionization technique. The excitation energy of the $3d$ state is 8.27 eV¹ and the first ionization potential (I.P.) is at 9.85 eV.^{1(b)}

A useful technique for probing the nature of electronic transitions is the method of variable-angle electron energy-loss spectroscopy. When an electron scatters from and ex-

cites an atom or molecule two mechanisms of electronic excitation are possible. The first is the long-range Coulomb excitation and is caused by the electric field produced when an electron passes the target. The differential cross section (DCS) for a transition excited in this manner exhibits a maximum at the scattering angle $\theta = 0^\circ$ (no change in direction) and decreases by approximately two orders of magnitude as θ increases from 0° to 90° .^{5,6} The second mechanism of electronic excitation involves the physical exchange of the incident electron with a target electron. The incident electron may exchange with a target electron of either the same or opposite spin; the former exchange process may or may not result in target excitation while the latter results in excitation to a spin-forbidden state. Transitions excited primarily by this mechanism possess a nearly uniform DCS as a function of scattering angle due to the loss of directional information carried by the incident electron.^{5,6}

With the above considerations in mind a variable-angle electron energy-loss spectroscopy study was undertaken of the polyatomic free radical CH₃. It was hoped that this investigation would yield information about possible low-lying spin-forbidden transitions. Previous electron spectroscopy of free radicals had been limited to stable species that were triatomic or smaller; e.g., the electron spectroscopy and differential cross sections have been determined for doublet-doublet allowed and doublet-quartet forbidden transitions in NO₂ by Rianda *et al.*⁷ The present paper reports the first electron-impact spectroscopy investigation of a transient polyatomic free radical.

II. EXPERIMENTAL

The spectrometer used in the present experiments has been described previously.⁸ Briefly, electrons are emitted from a tungsten filament and focused into a hemispherical monochromator. The monoenergetic electrons are then focused into the scattering region and, after interaction with the target molecules, enter a hemispherical analyzer prior to detection.

In order to generate the methyl radicals for the study, an

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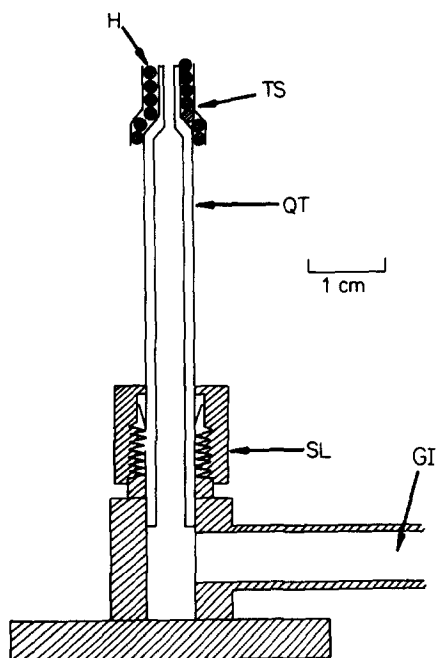


FIG. 1. Schematic diagram showing the free radical beam source. GI: gas inlet; H: heater; QT: quartz tube; SL: swagelock fitting; TS: tantalum shield.

in situ pyrolysis technique was employed.^{8(b)} A quartz tube of 0.060 in. i.d. with an outer layer of stainless steel sheathed heater wire (Fig. 1) produces an effusive jet of molecules. Pyrolysis temperatures of up to 800 °C, as measured by a thermocouple placed on the tube's outer surface, were used in these experiments.

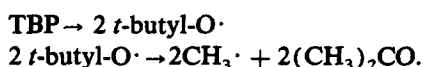
Three sources of methyl radicals were investigated. The first was tetramethyl tin (Aldrich, 99%), known to be a reliable source of methyl radicals.⁹ Taylor and Milazzo¹⁰ found a 30% conversion of tetramethyl tin at ≈ 600 °C, with 20% of the organic products existing as CH₃. Using our inlet, temperatures of ≈ 800 °C were required to achieve appreciable decomposition. Unfortunately after 5 h of continuous operation the quartz capillary became obstructed with metallic tin.

A second source of methyl radicals that was tried was ethyl nitrite. It is known that ethyl nitrite thermally decomposes by the reaction¹¹



The gaseous ethyl nitrite was synthesized by mixing ethanol (U. S. Industrial Chemicals Co., anhydrous) and isoamyl nitrite (Aldrich, 97%) in a 2:1 ratio by volume; an ester alcoholysis takes place producing isoamyl alcohol and continuously bubbling ethyl nitrite.¹² A pyrolysis temperature of 450 °C was used for the decomposition.

The third source of methyl radicals used was di-*t*-butylperoxide (Columbia Organic Chemicals Co., Inc.). It has been shown^{13,14} that the decomposition of di-*t*-butylperoxide (TBP) proceeds according to the following scheme:



Since this was the precursor that was used for nearly all of the investigation, an optimization of the temperature

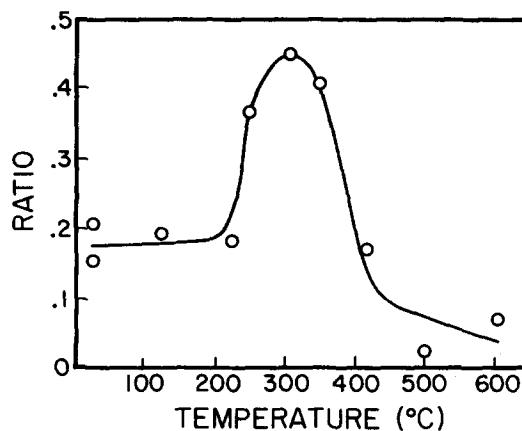


FIG. 2. Graph of the ratio of integrated intensity for the methyl 3s Rydberg transition at 5.73 eV to the acetone 3s Rydberg transition at 6.36 eV as a function of temperature. $E_0 = 50$ eV, $\theta = 10^\circ$.

needed for methyl production was carried out. The ratio of the methyl peak intensity at 5.73 eV to the acetone peak intensity at 6.36 eV vs temperature was examined at an incident electron energy $E_0 = 50$ eV and scattering angle $\theta = 10^\circ$ (Fig. 2). The ratio was found to possess a maximum at 300 ± 50 °C and this temperature was used in all subsequent studies. The number density of methyl radicals in the jet at this temperature was estimated to be 10^{13} molecule/cm³, on the basis of the intensity of the 5.73 eV band.

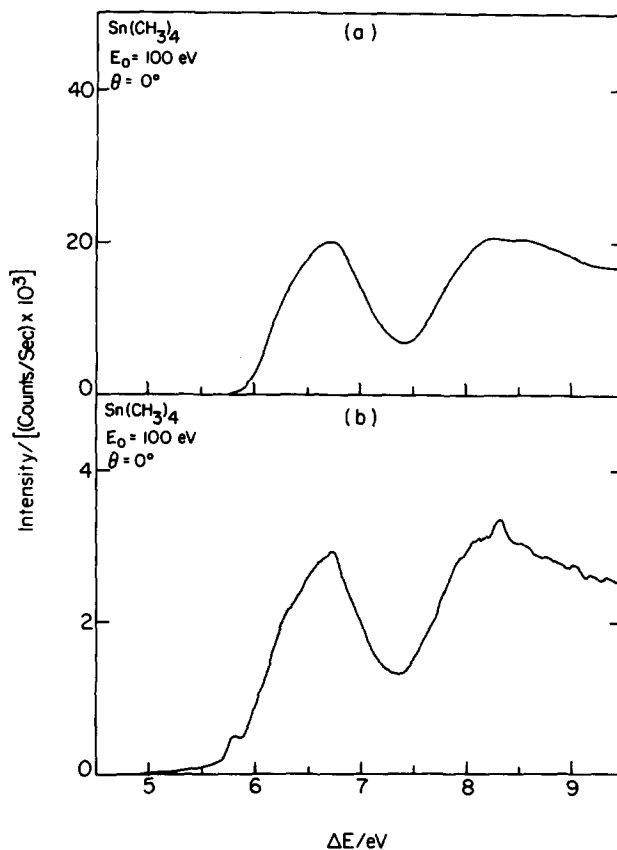


FIG. 3. Energy-loss spectrum of tetramethyl tin with (a) pyrolysis source off, (b) pyrolysis source on, $T = 800$ °C. For both spectra $E_0 = 100$ eV, $\theta = 0^\circ$. Incident electron current = 5 nA, estimated sample pressure = 1 mTorr.

III. RESULTS AND DISCUSSION

In Fig. 3 are shown two electron-impact spectra taken at $E_0 = 100$ eV and $\theta = 0^\circ$ between 4.5 and 9.5 eV energy loss. Figure 3(a) is the spectrum of tetramethyl tin obtained using the pyrolysis source at room temperature. It consists of two broad features with an onset at 5.7 eV and maxima at 6.71, 8.24, and 8.57 eV. Only two previous spectra for this compound have been reported. The first describes merely a continuum with an onset at 5.6 eV rising up to 6.2 eV.¹⁵ The second shows a maximum at 6.7 eV and ends at 7.1 eV.¹⁶ Ours is the first reported UV spectrum of this compound extending to the first I.P., located at about 9.7 eV.¹⁷ Intense $3s$ Rydberg transitions are known to occur in molecules with T_d symmetry if the originating orbital is of t_2 type.¹⁸ In this case the 6.71 and 8.24 eV features can be fit to the first two members of a Rydberg series with a quantum defect of 0.84 and I.P. = 9.62 eV. Figure 3(b) shows the same spectral region of the compound with the source heated to 800 °C. Immediately apparent are the sharp transitions located at 5.70, 8.30, and 8.98 eV. The 5.70 eV transition is assigned to the methyl $A''_2 3s$ Rydberg excitation. The 8.30 and 8.98 eV transitions are assigned to the $3d$ and $4d$ Rydberg excitations, respectively. Also of interest is the shoulder extending from 4.90 to 5.75 eV not present in the room temperature spectrum. It is possible that this shoulder is due to incompletely dissociated tetramethyl tin.

As stated previously, operation of the source with tetramethyl tin was limited to about 5 h. In addition, the lowest allowed methyl transition strongly overlapped with the lowest band of the compound, making DCS measurements more difficult. A second precursor that was investigated was ethyl

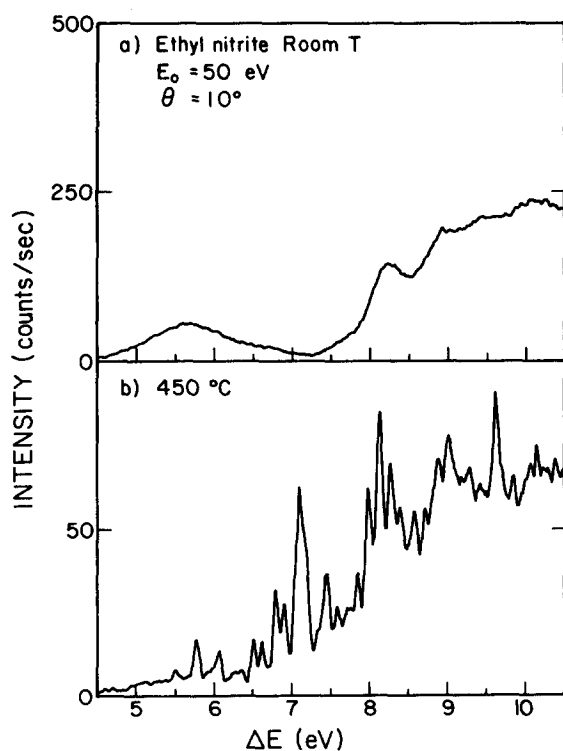


FIG. 4. Energy-loss spectrum of ethyl nitrite with (a) pyrolysis source off, (b) pyrolysis source on, $T = 450$ °C. For both spectra $E_0 = 50$ eV, $\theta = 10^\circ$. Incident electron current = 10 nA, estimated sample pressure = 1 mTorr.

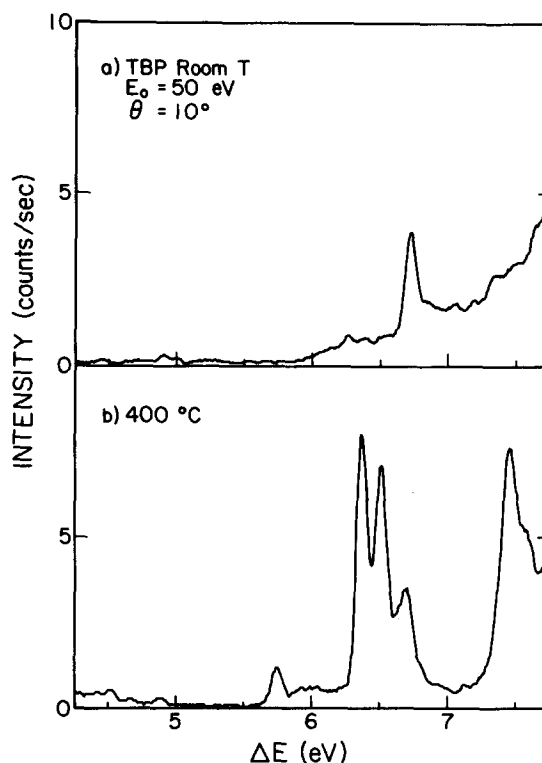


FIG. 5. Energy-loss spectrum of TBP with (a) pyrolysis source off, (b) pyrolysis on, $T = 400$ °C. For both spectra $E_0 = 50$ eV, $\theta = 10^\circ$. Conditions same as Fig. 4.

nitrite. It was expected that there could be much overlap of the methyl bands with the spectral features arising from the additional products NO and formaldehyde, and this was indeed found to be the case. Figure 4(a) shows the spectrum of ethyl nitrite without heating. It consists of several broad structureless features. Previous studies^{19,20} have only examined the lowest band in the region between 3.10 and 4.09 eV,^{14,19} not shown in Fig. 4(a). Peaks are observed at 5.69, 6.70, 7.76, 8.24, 8.94, 9.44, and 9.76 eV. In analogy with results for methyl nitrite²¹ the transition at 5.69 eV is assigned as $\pi \rightarrow \pi^*$ from an OCH_2CH_3 localized orbital to a NO localized orbital. The remaining bands are probably attributable to Rydberg transitions. Figure 4(b) shows the spectrum of the pyrolyzed ethyl nitrite; the spectrum is highly congested. No feature can be definitively attributed to a known methyl radical feature; every peak in the spectrum can be assigned to either NO²² or formaldehyde.^{23,24} One interesting observation is that the intensities of two $\gamma(A^2\Sigma^+ \leftarrow X^2\Pi)$ features at 5.92 and 6.27 eV are much larger with respect to the nearby $\beta(B^2\Pi \leftarrow X^2\Pi)$ peaks (at 5.47, 5.75, 6.04, and 6.33 eV) than previously reported.^{25,26} In fact, under conditions of similar incident electron energy and scattering angle the height of the transition at 6.27 eV is only about 10% of the height of the 6.34 eV transition.^{25,26}

The precursor molecule that was finally used to generate methyl radicals was TBP. Figure 5(a) shows a spectrum of TBP between 4.25 and 7.75 eV energy loss at $E_0 = 50$ eV and $\theta = 10^\circ$ at room temperature. It consists of a rising continuum with very little structure visible (the sharp feature at 6.67 eV is due to a Hg contamination). In Fig. 5(b) is shown

TBP at a pyrolysis temperature of 400 °C (results obtained prior to temperature optimization). The spectrum is drastically different and, as expected, most of the features are due to the pyrolysis product acetone with the exceptions being the sharp peak at 5.74 eV and the broad feature between 5.8 and 6.3 eV. The peak at 5.74 eV is again attributed to the methyl 3s Rydberg transition.

To help confirm the nature of the methyl transition an angular study was conducted. Figure 6(a) again shows the spectrum of TBP at $E_0 = 50$ eV and $\theta = 10^\circ$ between 5.6 and 6.4 eV energy loss and at the optimum temperature of 300 °C. In contrast, the spectrum of TBP under the same conditions at $\theta = 60^\circ$ is shown in Fig. 6(b). It is apparent that no drastic changes occur, although the ratio of the methyl 3s Rydberg transition to the acetone singlet-singlet A_1 3s transition at 6.36 eV goes from approximately 1:2 to 1:3. Increasing the angle further to 90° produces a change in this ratio back to about 1:2; however, due to the increase in the relative intensity of the intervening region of the spectrum the methyl peak is obscured. Most of the increase in the relative intensity between 5.8 and 6.3 eV is due to the presence of the singlet-triplet $\pi \rightarrow \pi^*$ band of acetone. As previously discussed, the intensity of such spin-forbidden bands is constant with angle while the intensity of fully allowed bands decreases with angle, thus the relative increase in the acetone singlet-triplet $\pi \rightarrow \pi^*$ band.

The DCS curves plotted in Fig. 7 illustrate the integrat-

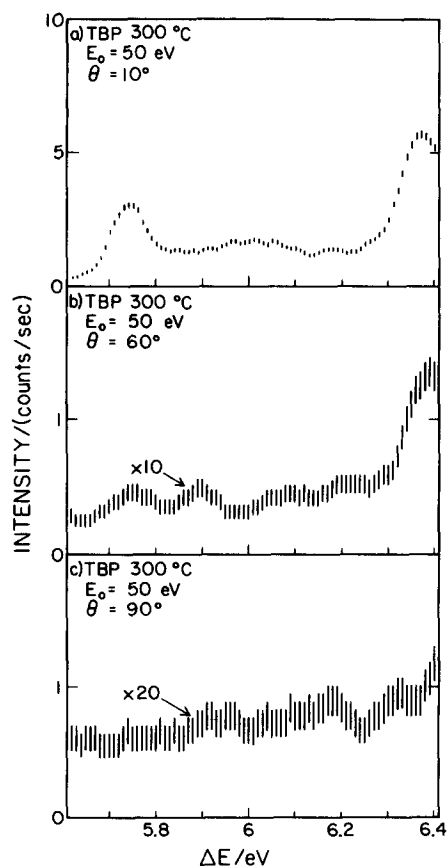


FIG. 6. Energy-loss spectrum of TBP at a pyrolysis temperature of 300 °C and $E_0 = 50$ eV: (a) $\theta = 10^\circ$, (b) $\theta = 60^\circ$, (c) $\theta = 90^\circ$. Conditions same as Fig. 4. Vertical lines indicate magnitude of error in spectral intensity.

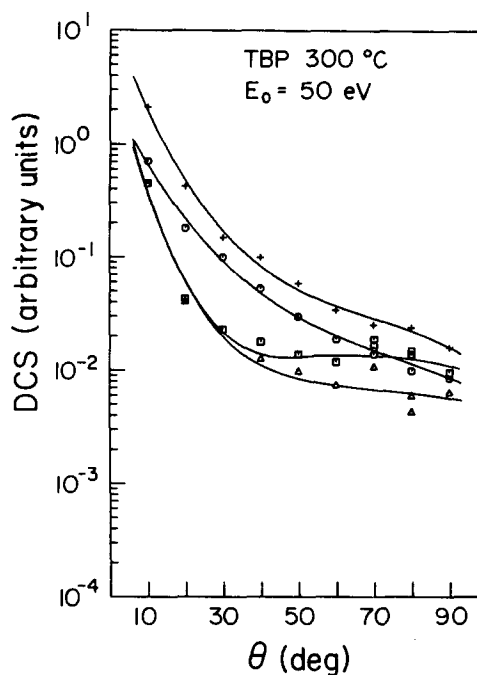


FIG. 7. DCS plot of pyrolyzed TBP, $E_0 = 50$ eV. Elastic scattering (EP) $\times 0.1$: +, acetone 3s $\times 100$: O, methyl 3s Rydberg $\times 100$: \square , corrected methyl 3s Rydberg (corrected by subtracting contribution of acetone spin-forbidden band) $\times 100$: \triangle . Arbitrary units are the same for all curves, which are multiplied by scaling factor before plotting.

ed intensity changes for these bands. The elastic peak and the acetone $n \rightarrow 3s$ peak exhibit an intensity decrease of about two orders of magnitude as should fully allowed bands. The methyl A_2'' 3s Rydberg band seems to be exhibiting this behavior also, but the curve begins to become more constant

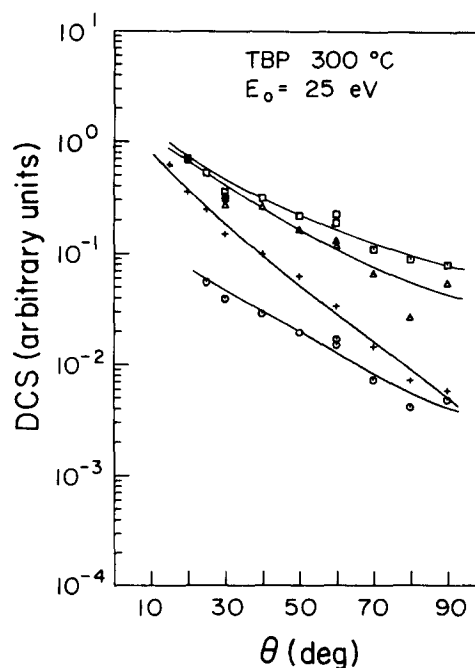


FIG. 8. DCS plot of pyrolyzed TBP, $E_0 = 25$ eV. EP $\times 0.1$: +, acetone 3s Rydberg $\times 100$: O, methyl 3s Rydberg $\times 1000$: \square , corrected methyl 3s Rydberg $\times 1000$: \triangle .

starting at $\theta = 60^\circ$. This is the angle where the spin-forbidden $\pi \rightarrow \pi^*$ band of acetone begins manifesting itself more strongly and, if this effect is subtracted out using the known angular behavior of this acetone band²⁴ and the acetone 3s Rydberg transition as a scaling feature, the DCS curve behaves more like a fully allowed band. At $E_0 = 50$ eV there seems to be little contribution from a spin-forbidden transition in methyl in the region of the $A_2''3s$ Rydberg band.

For CH₃ one would probably expect no low-lying spin-forbidden bands to be in evidence. All transitions from the highest occupied a_2'' orbital are spin allowed because the electron is unpaired. Likewise, only a spin-allowed version of the predicted lowest valence transition is possible. This contrasts with allowed Rydberg transitions converging to the second I.P. which would have spin-forbidden counterparts. A calculation by Millie and Berthier²⁷ places the second I.P. approximately 5 eV higher than the first I.P. Thus a spin-allowed excitation from the $2e'$ orbital to the $3s$ orbital would lie at about 10.5 eV and the spin-forbidden excitation at about 9.5 eV, allowing a double-quartet splitting of 1 eV (as Brongersma and Oosterhoff²⁸ found for the 3s Rydberg transition from a corresponding orbital in methane).

Another angular study was performed with the incident energy lowered to $E_0 = 25$ eV (Fig. 8). In this case the behavior is not as marked; however, the general trend suggesting that there is no spin-forbidden contribution to the methyl spectrum in the vicinity of the $A_2''3s$ Rydberg band is confirmed.

IV. SUMMARY

The spectra of three pyrolytic sources of methyl radicals (tetramethyl tin, ethyl nitrite, di-*t*-butyl-peroxide) were investigated by variable-angle electron energy-loss spectroscopy, both at room temperature and elevated temperatures. Of the three precursors, di-*t*-butyl-peroxide was found to be the most useful for radical generation. The spectrum of the decomposition co-product acetone has only moderate overlap with that of methyl and also is fairly well understood so that its effect can be removed. Regarding the 3s Rydberg excitation in CH₃, it has been found to possess a DCS in accord with the fully allowed nature.

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