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# The Near Ultraviolet Absorption Spectrum of Toluene Vapor

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The experimental work of Savard and the theoretical work of Sponer on the absorption spectrum of toluene vapor is extended. A spectrum of 209 bands was observed with partial resolution of the fine structure. A tentative analysis is given based on ground state frequencies 514, 620, 785, 1003, 1012, 1176, and 1209, which correlate completely with Raman data; on excited state frequencies, 456, 528, 751, 932, 964, and 1186; and on difference frequencies 59 and 178 cm$^{-1}$. Assuming $C_{2v}$ symmetry, all frequencies below 1300 cm$^{-1}$ of symmetry class $A_1$ appeared in $1-0$ transitions and with one exception in $0-1$ transitions. In addition, a vibrational frequency of symmetry class $B_1$, deriving from an $\epsilon_g^+$ vibration in benzene, appeared strongly both in the ground and excited state.

## INTRODUCTION

THIS investigation is a continuation of the study of the effect of substituents on the near ultraviolet absorption spectrum of the benzene nucleus. The substituents previously studied, Cl,[1] NH$_2$,[2a] OH,[2b] and F,[3] all possess an unshared pair of electrons which can resonate with the nucleus to modify rather markedly the electronic structure; in addition to this, an inductive effect of smaller magnitude operates.[4] It was of interest, therefore, to investigate the effect of the substitution of the CH$_3$ group, which does not possess an unshared pair of electrons to resonate with the ring. However, Mulliken, Rieke, and Brown[5] have pointed out the possibility of resonance due to hyperconjugation of the methyl group with the benzene nucleus. It is expected that this resonance will modify the electronic structure of the benzene nucleus to a lesser extent than that mentioned above.

Sponer[6] has discussed the theory and has analyzed Savard's[7] data on toluene assigning a large number of fundamental vibration frequencies in the excited state. Masaki[8] who also investigated the absorption of toluene, reported only the wave numbers of the $0-0$ and four $1-0$ bands. The Raman data have been summarized by Kohlrausch and Wittek[9] and by Pitzer and Scott,[10] the latter having completely classified the Raman frequencies.

In the present investigation the absorption spectrum of toluene was studied under higher dispersion and with greater resolving power than previously. A partial resolution of the fine structure, as well as the observation of a number of new bands resulted. Further, it was possible to obtain additional fundamental vibration frequencies in both the ground and excited states, to make a number of additional assignments, and to associate the fundamental frequencies with definite modes of vibration, this latter resulting from a complete correlation with Raman data.

## EXPERIMENTAL

The absorption spectrum of toluene lies in the region 2390–2760A. All measurements were made in the second order of a spectrograph of the Eagle type, with a 3-meter grating ruled 15,000 lines per inch. The light source was a 5000-volt,

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[2a] N. Ginsburg and F. A. Matsen, J. Chem. Phys. **13**, 167 (1945).
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[9] K. W. F. Kohlrausch and H. Wittek, Monatsh **74**, 1 (1941).
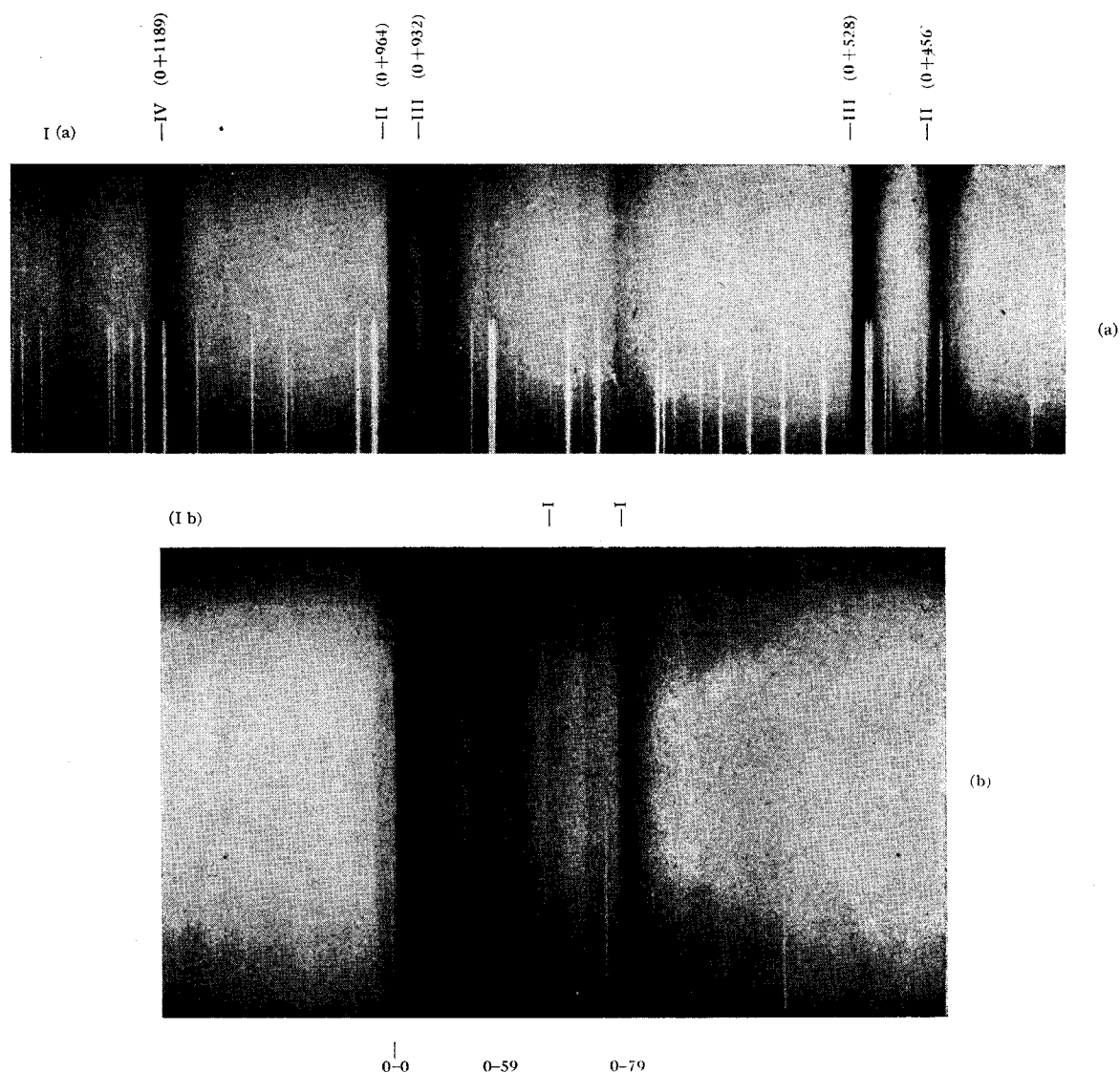[10] K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. **65**, 803 (1943).

FIG. 1. The four different types of bands in the absorption spectrum of toluene, (a) in the region 2585–2635Å and (b) in the region 2667–2680Å.

2.5-kva hydrogen discharge tube, and the spectrum was photographed on Eastman 103−0 and 103−0 UV-sensitized plates.

Two absorption cells were used, one of 12-cm length, the other 70-cm, both all quartz. The shorter cell was used in almost all exposures, the long cell being necessary only for extreme development of the spectrum. The amount of toluene vapor introduced into the cells was controlled by variation of the temperature of the reservoir containing the toluene liquid. This was varied between −20° and 24°C for the short cell

and between 0°C and 50°C for the long cell. The cell was heat. d to the same temperature as the reservoir when the reservoir was above room temperature.

Sulfur-free toluene with a 1°C boiling range was obtained from Eastman Kodak. It was redistilled in a meter-long, packed, adiabatic column. A number of cuts were taken and the cut with the highest refractive index ($n_D^{20°} = 1.4952$, BP. = 109.7°C at 745 mm) was retained for this investigation.

The 209 bands observed were measured to an

accuracy of 0.3 cm$^{-1}$ for the very sharp bands, with the accuracy diminishing to 3 cm$^{-1}$ for the extremely diffuse bands. Four types of band structure were observed: (I) doublets with the components of equal intensity; (II) doublets with a strong, long wave-length component and weak, short wave-length component; (III) bands with sharp heads with no apparent doublet structure and degraded toward the red; and (IV) diffuse bands with no sharp heads and most intense in the center (Fig. 1). This varied character made it necessary to set the cross-hair of the comparator at different relative positions for the different types of bands. The first two types were measured at the centers of gravity of the components of the doublets. The last two types were measured to the sharp head and the apparent head, respectively. Types II and IV were not found in aniline[2a] and phenol.[2b] The roman numeral in Table I indicates the type of band.

## THEORY

Sponer[6] has pointed out that the spectrum of toluene, like that of other mono-substituted benzenes, possesses certain features of the benzene spectrum as well as other features arising from the reduction of the symmetry from type $D_{6h}$ to a lower symmetry type. This reduction in symmetry makes allowed the forbidden (in benzene) $0-0$ and other transitions involving only totally symmetric frequencies.

Sponer assigned $C_s$ symmetry to toluene. However, if one considers the effect of the methyl group on the benzene ring the same as that of a one-atom substitution, toluene may be assigned a symmetry $C_{2v}$ as has been done by Pitzer and Scott in their discussion of the Raman data. Then, by analogy with the Sponer-Wollman treatment of chlorobenzene, the electronic transition is $A_1-B_1$, the electric moment lying in the $y$ direction, that is in the plane of the ring perpendicular to the $z$ axis, which lies along the $CH_3-C$ bond. This transition is allowed as are transitions involving vibrational states of symmetry class $A_1$. This transition is also allowed when vibrational states of symmetries $B_1$ and $A_2$ are excited. Such vibronic transitions, however, give rise to moments in the $x$ and $z$ directions, which are not believed to participate strongly. Hence, vibrations of symmetry class $B_1$ and $A_2$

should appear only weakly if at all, since for a single quantum excitation the symmetry of the vibrational state is the same as that of the vibration.

When vibrations of symmetry class $B_2$ are superposed on the electronic transition $A_1-B_1$, the transition integral is not invariant for any of the three moments and these vibrations should not appear at all. $1-1$ transitions for vibrations of any symmetry class are allowed.

It is to be expected, however, that some aspects of the benzene spectrum are to be carried over into the spectrum of toluene, since the methyl group perturbation on the benzene ring cannot be very great. Hence the analog of the relatively strong absorbing $\epsilon_g^+$ vibration which made the $A_{1g}-B_{2u}$ transition allowed in benzene, should appear strongly in the toluene spectrum. This in benzene is a degenerate vibration, whose degeneracy is removed as the symmetry of the molecule is reduced.

For $C_{2v}$ symmetry the degenerate $\epsilon_g^+$ vibration, 6a and 6b,[11] of $D_{6h}$ symmetry divides, the 6a vibration becoming a member of symmetry class $A_1$, while 6b becomes a member of $B_1$. Hence 6b should yield a strong band more intense than the other members of class $B_1$.

## DISCUSSION

The strongest band in the spectrum, the Type II doublet at 37,477 and 37,480 cm$^{-1}$, was taken to be the $0-0$ band. Savard[7] reports 37,473 cm$^{-1}$ for this band, while Masaki[8] reports 37,477 cm$^{-1}$. In addition to the $0-0$ doublet, there appears a satellite doublet nine wave numbers to the red, similar to the diffuse satellite observed in chlorobenzene, aniline, and phenol.

The frequencies of the bands on the long wave-length side of the $0-0$ band which correspond to reported Raman frequencies are given in Table II. The characterization numbers are those from Pitzer and Scott[9] and correspond to the usual numbering of the benzene frequencies. Six out of twelve possible non-totally symmetric frequencies were observed which could be correlated with reported Raman frequencies. The five starred in the table are of doubtful correlation. Of these five, two ($M6$ and 17a) are correlations

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TABLE I. The absorption spectrum of toluene. The intensities are designated as $vvw$ = extremely weak, $vw$ = very weak, $w$ = weak, $m$ = medium, $ms$ = medium strong, $s$ = strong, $vs$ = very strong, $vvs$ = extremely strong, $B$ = broad, and $D$ = diffuse. Primed intensities indicate measurements to the head of the band. $(S)$ = satellite.

| Wave-length (Ang-stroms) | Wave number | Intensity | Type | Assignment | Wave-length (Ang-stroms) | Wave number | Intensity | Type | Assignment |
|---|---|---|---|---|---|---|---|---|---|
| 2756.4 | 36,268 | $vvw'$ | III | $0-1209$ | 2670.7 | 37,432 | $vvw$ | | $0-1012+964$ |
| 2754.0 | 36,301 | $vvw'$ | III | $0-1004-178$ $0-1176$ | 2668.28 | 37,466.2 | $s$ | I | $0-0-9$ $(S)$ |
| 2745.3 | 36,415 | $vvw'$ | III | $0-1003-59$ | 2667.96 | 37,470.7 | $s$ | | |
| 2741.5 | 36,465 | $vvwBD$ | | $0-1012$ | 2667.48 | 37,477.4 | $vvs$ | II | $0-0$ |
| 2740.9 | 36,474 | $vwBD$ | | $0-1003$ | 2667.27 | 37,480.4 | $s$ | | |
| 2739.5 | 36,493 | $vvwBD$ | | | 2666.3 | 37,495 | $vw$ | | |
| 2737.6 | 36,517 | $vvwBD$ | | $0-785-178$ | 2663.2 | 37,538 | $vw$ | | |
| 2735.7 | 36,543 | $vvwBD$ | | | 2655.3 | 37,649 | $vw$ | | |
| 2733.6 | 36,571 | $vvwBD$ | | | 2651.3 | 37,706 | $vvw$ | | $0-520+751$ |
| 2732.1 | 36,591 | $vvw$ | | | 2648.4 | 37,748 | $vvw$ | | |
| 2729.06 | 36,631.8 | $vvw$ | I | $0-785-59$ | 2647.5 | 37,760 | $vw$ | | $0+456-178$ |
| 2728.69 | 36,636.8 | $vvw$ | | | 2645.8 | 37,785 | $vvwBD$ | | $0-620+931$ |
| 2725.95 | 36,673.2 | $vvw$ | I | $0-620-178$ | 2644.1 | 37,823 | $w$ | | $0+964-620$ |
| 2725.77 | 36,676.0 | $vvw$ | | | 2642.71 | 37,828.7 | $w$ | I | $0+528-178$ |
| 2724.56 | 36,692.3 | $w$ | I | $0-785$ | 2642.51 | 37,831.6 | $w$ | | |
| 2724.25 | 36,690.5 | $vw$ | | | 2641.3 | 37,850 | $vvwBD$ | | |
| 2723.6 | 36,705 | $vvwBD$ | | | 2640.6 | 37,859 | $vw'$ | III | |
| 2721.9 | 36,729 | $vvw$ | | $0-1209+456$ | 2639.7 | 37,872 | $vw$ | | |
| 2721.4 | 36,735 | $vvw$ | | | 2639.5 | 37,875 | $vw$ | | $0+456-59$ |
| 2719.3 | 36,763 | $vvw'$ | III | | 2636.8 | 37,913 | $mBD$ | | |
| 2717.71 | 36,784.8 | $vw'$ | III | $0-514-178$ | 2636.1 | 37,924 | $mBD$ | | $0+964-520$ $0+456-9$ $(S)$ |
| 2716.9 | 36,796 | $vw$ | | $0-620-59$ | 2635.40 | 37,933.6 | $s$ | II | $0+456$ |
| 2715.82 | 36,810.4 | $vvw$ | I | | 2635.17 | 36,936.9 | $m$ | | |
| 2715.56 | 36,813.9 | $vvw$ | | | 2634.35 | 37,948.7 | $w$ | I | $0+528-59$ |
| 2712.35 | 36,857.5 | $w'$ | III | $0-620$ | 2634.05 | 37,953.1 | $m$ | | |
| 2711.3 | 36,872 | $vvwB$ | | | 2632.0 | 37,982 | $vwD$ | | |
| 2709.28 | 36,899.2 | $vvw$ | I | $0-514-59$ | 2631.65 | 37,987.7 | $w$ | I | |
| 2709.00 | 36,903.1 | $vvw$ | | | 2631.43 | 37,992.3 | $w$ | | |
| 2704.59 | 36,963.2 | $w'$ | | $0-514$ | 2631.25 | 37,993.4 | $s$ | I | $0+528-9$ $(S)$ |
| 2693.1 | 37,121 | $vvw$ | | $0-2\times178$ | 2630.88 | 37,998.8 | $s$ | | |
| 2690.9 | 37,151 | $vvw$ | | $0-785-456$ | 2630.45 | 38,005.0 | $vs$ | I | $0+528$ |
| 2688.0 | 37,191 | $vvw$ | | | 2630.23 | 38,008.2 | $vs$ | | |
| 2686.9 | 37,206 | $vvw$ | | | 2630.10 | 38,010.0 | $vs$ | | |
| 2684.1 | 37,245 | $vw$ | IV | $0-178-59$ | 2629.5 | 38,019 | $vvwD$ | | |
| 2681.42 | 37,282.6 | $vw$ | I | | 2625.3 | 38,080.1 | $vvwBD$ | | |
| 2681.20 | 37,285.7 | $vw$ | | | 2623.6 | 38,104 | $vwBD$ | | |
| 2680.87 | 37,290.3 | $vw$ | I | | 2618.9 | 38,173 | $vvw$ | | $0+751-59$ |
| 2680.62 | 37,293.7 | $vw$ | | | 2616.2 | 38,212 | $wD$ | | |
| 2680.21 | 37,299.4 | $ms$ | I | $0-178$ | 2615.08 | 38,228.3 | $m$ | I | $0+751$ |
| 2680.01 | 37,302.2 | $ms$ | | | 2614.87 | 38,231.4 | $m$ | | |
| 2679.9 | 37,304 | $vw$ | | $0-3\times59$ | 2614.76 | 38,233.0 | $m'$ | III | $0+932-178$ |
| 2679.04 | 37,315.7 | $vw$ | I | | 2612.93 | 38,259.8 | $w$ | I | $0+964-78$ |
| 2678.76 | 37,319.6 | $vw$ | | | 2612.70 | 38,263.2 | $w$ | | |
| 2678.31 | 37,325.9 | $vw$ | I | | 2611.4 | 38,282 | $vw$ | | |
| 2678.09 | 37,329.0 | $vw$ | | | 2610.63 | 38,293.5 | $vw'$ | III | $0+932-2\times59$ |
| 2677.1 | 37,343 | $vvw$ | | | 2608.99 | 38,317.6 | $vvw$ | I | $0+964-2\times59$ |
| 2676.10 | 37,356.7 | $w$ | I | $0-2\times59$ | 2608.73 | 38,321.4 | $vvw$ | | |
| 2675.80 | 37,360.9 | $w$ | | | 2607.3 | 38,342 | $vwD$ | | |
| 2674.30 | 37,381.9 | $w$ | I | $0-620+528$ | 2606.71 | 38,351.1 | $m$ | II | $0+932-59$ |
| 2674.12 | 37,384.4 | $w$ | | | 2606.48 | 38,354.8 | $w$ | | |
| 2673.76 | 37,389.4 | $vvw$ | I | | 2606.1 | 38,361 | $vvw$ | | |
| 2673.49 | 37,393.2 | $vvw$ | | | 2604.6 | 38,382 | $mBD$ | | $0+964-59$ |
| 2671.72 | 37,418.0 | $ms$ | I | $0-59$ $0-514+456$ | 2604.0 | 38,391 | $vw$ | | $0+2\times456$ |
| 2671.48 | 37,421.3 | $ms$ | | | | | | | |

TABLE I.—*Continued.*

| Wave-length (Ang-stroms) | Wave number | Intensity | Type | Assignment | Wave-length (Ang-stroms) | Wave number | Intensity | Type | Assignment |
|---|---|---|---|---|---|---|---|---|---|
| 2603.2 | 38,402 | $mBD$ | | $0+932-9$ $(S)$ | 2541.45 | 39,335.8 | $vw'$ | III | $0+2\times932-9$ $(S)$ |
| 2602.76 | 38,409.3 | $vs$ | I | $0+932$ | 2541.11 | 39,341.1 | $m$ | I | $0+2\times932$ |
| 2602.60 | 38,411.6 | $vs$ | | | 2540.96 | 39,343.4 | $m$ | | |
| 2602.46 | 38,413.7 | $m'$ | III | | 2539.5 | 39,367 | $mBD$ | | $0+932+964-9$ $(s)$ |
| 2601.3 | 38,431 | $mBD$ | | $0+964-9$ $(S)$ | 2538.90 | 39,375.3 | $msD'$ | III | $0+932+964$ |
| 2601.0 | 38,435 | $msD$ | | | 2538.8 | 39,377 | $w$ | | |
| 2600.59 | 38,441.3 | $s$ | II | $0+964$ | 2537.9 | 39,391 | $wB$ | | |
| 2600.36 | 38,444.7 | $m$ | | | 2536.92 | 39,406.0 | $m'$ | III | $0+2\times964$ |
| 2599.6 | 38,456 | $vwBD$ | | | 2534.0 | 39,452 | $vw$ | | |
| 2597.6 | 38,486 | $vwBD$ | | $0+1189-178$ | 2531.6 | 39,489 | $vvw$ | | |
| 2596.1 | 38,508 | $vvwBD$ | | | 2530.1 | 39,513 | $vwBD$ | | $0+2\times751+528$ |
| 2595.9 | 38,512 | $vw$ | | | 2528.8 | 39,532 | $vvwBD$ | | |
| 2594.0 | 38,539 | $vvw$ | | $0+2\times528$ | 2528.1 | 39,543 | $vw$ | | |
| 2593.4 | 38,547 | $vvwBD$ | | $0+1189-2\times59$ | 2526.8 | 39,563 | $vvw$ | | |
| 2592.7 | 38,559 | $vvwBD$ | | | 2524.4 | 39,602 | $ms'$ | IV | $0+1189+932$ |
| 2592.3 | 38,565 | $vvw$ | | | 2522.2 | 39,636 | $s'$ | IV | $0+1189+964$ |
| 2591.5 | 38,577 | $vvwD$ | | | 2520.6 | 39,662 | $vw$ | | |
| 2591.1 | 38,582 | $vw$ | | | 2519.9 | 39,672 | $vwBD$ | | |
| 2589.9 | 38,601 | $wBD$ | | | 2518.60 | 39,692.7 | $m'$ | III | $0+528+751+932$ |
| 2589.3 | 38,610 | $wBD$ | | $0+1189-59$ | 2517.5 | 39,712 | $wB$ | | |
| 2585.5 | 38,666 | $s'$ | IV | $0+1189$ | 2516.6 | 39,725 | $w$ | | $0+528+751+964$ $0+2\times528+1189$ |
| 2585.05 | 38,672.4 | $ms'$ | III | | | | | | |
| 2582.86 | 38,705.2 | $vw'$ | III | | 2513.0 | 39,782 | $vw'$ | IV | |
| 2580.62 | 38,738.8 | $m'$ | III | | 2511.80 | 39,800.1 | $w'$ | III | $0+457+2\times932$ |
| 2579.9 | 38,749 | $wBD$ | | $0+751+528-9$ $(S)$ | 2511.1 | 39,811 | $vwD$ | | |
| 2579.41 | 38,757.0 | $m$ | I | $0+751+528$ | 2509.59 | 39,835.2 | $w'$ | III | $0+457+932+964$ |
| 2579.24 | 38,759.5 | $m$ | | | 2508.5 | 39,853 | $wD$ | | $0+2\times1189$ |
| 2577.0 | 38,794 | $vw'$ | IV | | 2507.22 | 39,872.8 | $m'$ | III | $0+528+2\times932$ |
| 2576.2 | 38,805 | $vvwBD$ | | | 2505.28 | 39,903.7 | $s'$ | III | $0+528+932+964$ |
| 2575.5 | 38,815 | $vwBD$ | | | 2503.6 | 39,930 | $wD$ | | $0+2\times964+528$ |
| 2574.3 | 38,834 | $vvw$ | | | 2502.7 | 39,945 | $vwBD$ | | $0+2\times751+964$ |
| 2573.4 | 38,840 | $m$ | | | 2490.8 | 40,135 | $w'$ | IV | $0+751+932+964$ $0+528+932+1189$ |
| 2571.92 | 38,869.8 | $m'$ | III | $0+932+457$ | | | | | |
| 2571.2 | 38,881 | $w$ | | | 2488.9 | 40,166 | $w'$ | IV | $0+2\times751+1189$ |
| 2567.75 | 38,932.9 | $w'$ | III | $0+932+528-9$ $(S)$ | 2480.3 | 40,306 | $wBD$ | | $0+2\times931+964$ |
| 2567.17 | 38,941.7 | $s'$ | III | $0+932+528$ | 2479.3 | 40,322 | $wD$ | | |
| 2565.9 | 38,960 | $wBD$ | | $0+964+528-9$ $(S)$ | 2478.4 | 40,337 | $wBD$ | | $0+2\times964+932$ |
| 2565.17 | 38,972.1 | $s'$ | III | $0+964+528$ | 2477.6 | 40,349 | $vvwBD$ | | $0+751+932+1189$ |
| 2564.4 | 38,984 | $w$ | | $0+2\times751$ | 2475.5 | 40,384 | $vvwBD$ | | $0+528+2\times1189$ $0+964+1189+751$ |
| 2560.0 | 39,051 | $vvw$ | | | | | | | |
| 2559.0 | 39,065 | $vvw$ | | $0+3\times528$ | 2465.03 | 40,555.2 | $s'$ | III | |
| 2556.9 | 39,099 | $vw$ | | | 2464.5 | 40,565 | $vw$ | | $0+932+964+1189$ |
| 2556.3 | 39,107 | $vw$ | | | 2449.3 | 40,816 | $vw$ | | $0+2\times1189+964$ |
| 2555.2 | 39,124 | $wBD$ | | $0+1189+457$ | 2446.7 | 40,859 | $vvw$ | | |
| 2553.87 | 39,144.5 | $vw$ | I | $0+2\times457+751$ | 2436.5 | 41,030 | $vvw$ | | |
| 2553.66 | 39,147.7 | $vw$ | | | 2421.9 | 41,278 | $vw$ | | |
| 2552.7 | 39,162 | $m$ | | $0+932+751$ | 2409.3 | 41,494 | $vw$ | | |
| 2550.0 | 39,204 | $s'$ | IV | $0+1189+528$ $0+964+751$ | 2395.3 | 41,736 | $vvw$ | | |

TABLE II. The fundamental frequencies of toluene. Raman frequencies beyond 1212 are not reported.
* Indicates doubtful correlation.

| Characterization No. | Raman Masaki | Ground State Pitzer Scott | Ground State Kohlrausch Wittek | Ultraviolet absorption Masaki | Ultraviolet absorption This research | Excited State This research | Savard (Sponer) |
|---|---|---|---|---|---|---|---|
| Symmetry $A_1$ | | | | | | | |
| 6a | 520 | 521 | 521 (6) | 517 | 514 $w$ | 456 $s$ | 466 |
| 12 | 786 | 785 | 786 (9) | 781 | 785 $vvw$ | 751 $m$ | — |
| 1 | — | 1002 | 1004 (12) | — | 1003 $vw$ | 932 $vs$ | 930 |
| 18a | — | 1030 | 1030 (8) | — | 1012 $vvw$ | 964 $s$ | 964 |
| 9a | — | 1175 | 1177 (1) | — | 1176 $vvw$ | | |
| 7a | — | 1210 | 1208 (5) | — | 1212 $vvw$ | 1189 $s$ | 1193 |
| Symmetry $B_1$ | | | | | | | |
| 18b | 333 | 340 | 344 ($\frac{1}{2}$) | 334 | — | | |
| 6b | 622 | 622 | 623 (4) | 623 | 620 $w$ | 528 $vs$ | 527 |
| M6 | — | 1060 | 1085 (0) | — | *1062 $vvw$ | | |
| 9b | — | 1155 | 1155 (2) | — | — | | |
| Symmetry $A_2$ | | | | | | | |
| 16a | — | 405 | 405 (0) | — | — | | |
| 10a | — | 842 | 843 (1) | — | *845 $vvw$ | | |
| 17a | — | (985) | 977 ($\frac{1}{2}$) | — | *988 $vvw$ | | |
| | | | 933 ($\frac{1}{2}$) | | | | |
| Symmetry $B_2$ | | | | | | | |
| 11 | — | 216 | 216 (5b) | — | — | | |
| 16b | — | 467 | — | — | — | | |
| 10b | — | 730 | 730 (1) | — | *714 $vvw$ | | |
| 17b | — | 890 | 897 (1b) | — | *886 $vvw$ | | |
| M6 | — | 1190 | 1189 (00) | — | — | | |
| Difference | | | | | 59 $ms$ | | |
| Frequencies | | | | | 178 $ms$ | | |

with rather doubtful Raman frequencies. 10a has a reasonable assignment in terms of symmetric frequencies. 10b and 17b may also be coincidences since vibration 11 (216 cm$^{-1}$), which is in the same symmetry class, $B_2$, is five times as intense in the Raman spectrum and has a large Boltzmann factor, does not appear. This leaves only the frequency 6b (620 cm$^{-1}$) as the one non-totally symmetric vibration which can be definitely assigned. Further, the fundamental frequency, 528, of the excited state could not be correlated with any ground state frequency other than 620. If this correlation is correct, the 6b frequency was the only non-totally symmetric fundamental frequency observed in the excited state. The absence of the non-totally symmetric vibrations (except 6b) is in accord with the theory given in the previous section. Vibrations of class $B_2$ are definitely forbidden. Vibrations of classes $A_2$ and $B_1$ (except 6b) may occur weakly according to the theory. The intensities of the corresponding Raman bands are very low and it is often found that very weak Raman frequencies do not appear in ultraviolet absorption.

The 6b vibration appears relatively strongly as 620 cm$^{-1}$ (Raman 622 cm$^{-1}$) in the ground state and very strongly as 528 in the excited state. Sponer did not list the ground-state frequency, but gave 527 for the excited state. This vibration is the $B_1$ component resulting from the removal of the degeneracy of the $\epsilon_g{}^+$ vibration (606 cm$^{-1}$ in benzene) upon the substitution of the methyl group. The 528 frequency combines strongly with all totally symmetric vibrations analogous to the situation in benzene. The band $0+2\times528$ appears only weakly in this spectrum. According to Herzberg and Teller[12] and Sponer and Teller,[13] non-totally symmetric vibrations have their minima above one another; hence, on the basis of the Franck-Condon principle the doubly excited frequency should be weak. Wollman[3] has pointed out that the doubly excited frequency becomes stronger in the order of increasing perturbing effect of halogen substituents on the ring Br<Cl<F.

Two strong low frequency "red" bands, 59

[12] G. Herzberg and E. Teller, Zeits. f. physik. Chemie B21, 410 (1933).
[13] H. Sponer and E. Teller, Rev. Mod. Phys. 13, 76 (1941).

and 178 cm$^{-1}$, which cannot be correlated with any single Raman frequency, appear. It must be concluded that these are $1-1$ transitions. No assignment could be made for the $0-178$ band on the basis of assigned fundamental frequencies. The $0-59$ band may be interpreted as $0-514+457$ since both $0-514$ and $0+457$ appear. Again, as in previous investigations, the presence of bands to which assignments $0-2\times59$ and $0-3\times59$ are made, may argue against such an assignment since $0-2\times514$ and $0-3\times514$ do not appear. Further, assuming that no change in transition probabilities is involved, the ratio of the intensities of the combination bands should be the ratio of the Boltzmann factors, $_e-514hc/kT:_e-2\times514hc/kT:_e-3\times514hc/kT$, or $1:0.083:0.0068$. The ratio of intensities obtained microphotometrically was $1:0.25$ with the third uncertain because it occurred on the shoulder of the strong $0-178$ band.

However, $1-1$ transitions are allowed even when the corresponding $0-1$ and $1-0$ transitions are forbidden. Thus, a $1-1$ transition involving frequency 11 (216 cm$^{-1}$) or symmetry class $B_2$ might account for the 59 cm$^{-1}$ series. It is to be noted that this vibration yields the most intense Raman band of all of the non-totally symmetric vibrations. The ratio of the Boltzmann factors for this vibration is $1:0.33:0.11$. Consequently, $0-216+157$ is a possible interpretation of the $0-59^{14}$ band.

The fundamental frequencies of the excited state are given in Table II. Those all appeared as doublets for the $0-1$ transitions. In addition there appeared a satellite band nine wave numbers toward the red for each of these transitions and for some of the combination bands similar to that mentioned above for the $0-0$ band and reported for some of the previously investigated mono-substituted benzenes. All totally symmetrical frequencies below 1300 cm$^{-1}$ have been identified in the excited state with the exception of 1176. This frequency yields a Raman band much less intense than yielded by any of the other totally symmetric frequencies.

In Table III are listed the differences between

TABLE III.

| Frequency | Frequency differences | |
| | Benzene Raman – Toluene Raman: | Toluene Raman – Toluene excited |
| --- | --- | --- |
| 7a | 1837 cm$^{-1}$ | 21 cm$^{-1}$ |
| 12 | 226 | 34 |
| 6a | 85 | 65 |
| 18a | 7 | 66 |
| 1 | −10 | 70 |
| 6b | −14 | 94 |

the Raman frequencies for benzene and toluene and between the Raman frequencies and excited state frequencies for the six totally symmetric frequencies identified in this research. Since the methyl group replaces a hydrogen atom it is expected that predominantly hydrogen vibrations will be more affected by the substitution than will the typically carbon vibrations. On the other hand, since the electronic excitation affects the $\pi$ electrons localized in the carbon-carbon bonds, it is to be expected that the typically carbon frequencies will be affected more in the excitation process. This is borne out by Table III.

Most of the $0+1\times\nu_i'\times1\times\nu_j'$ [15] bands were present with the exception of $0+456+1\times\nu_j'$, of which series only $\nu_j'=932$ and 1189 appear. The only other missing band of this type was $0+751+1189$. Of the transitions in which three quantum numbers change, only about half of the possible bands were found with no series appearing to be better than any other.

It may be concluded that the substitution of the CH$_3$ group affects the spectrum of the nucleus in much the same way as the substituents Cl, F, NH$_2$, and OH. However, the toluene spectrum is not as well developed for the transitions involving the higher vibrational quantum numbers as are the spectra of the latter. This may be attributed to the absence of an unshared pair of electrons on the CH$_3$ group.

[14] See the discussion of the corresponding frequency in chlorobenzene by Sponer and Wollman, reference 1.

[15] $\nu_i'$ and $\nu_j'$ represent frequencies (cm$^{-1}$) in the excited state.