Vibronic Selection Rules. The dominant fluorescence structure from every emitting level appears to be predicted simply. It will be that for which the e_{2g} mode ν_6 changes quantum number by ± 1 while $\Delta v = 0$ for all other modes except ν_1. Changes in ν_1 establish long progressions on the ν_6 transition. We have observed no exceptions to this pattern.

The remaining fluorescence transitions are generally at least an order of magnitude weaker. They derive intensity from first-order Herzberg–Teller transitions involving e_{2g} modes other than ν_6, or more commonly they represent a limited selection of second-order transitions. These are summarized in the section Vibronic Activity in the $^1B_{2u}$–$^1A_{1g}$ Transition.

Franck–Condon Factors. The fluorescence spectra offer an extended view of polyatomic Franck–Condon factors. Numerous spectra display the relative intensities in ν_1 progressions of the types 1^0_n and 1^1_n, and one spectrum shows the progressions 1^2_n. These three types are qualitatively different, and each matches the general expectations of approximate Franck–Condon calculations. The $\langle\phi_1''(1)|\phi_1'(1)\rangle$ overlap integral "cancellation" described by Smith is clearly seen. The great differences between 1^0_n, 1^1_n, and 1^2_n progression envelopes is a principal contributor to the unique appearance of individual SVL fluorescence spectra.

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(33) For example, see Figure 2 of ref 31.

(34) Fluorescence in higher members can be observed but well over 90% of a progression's intensity is contained in the first five members.

An Extended View of the Benzene 260-nm Transition via Single Vibronic Level Fluorescence. II. Single Vibronic Level Fluorescence as a Probe in the Assignment of the Absorption Spectrum[1,2]

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Abstract: Twelve regions of the benzene 260-nm transition have been probed with narrow-band excitation to produce fluorescence spectra from single vibronic levels or small groups of levels of the $^1B_{2u}$ state. The fluorescence analyses identify many of the emitting levels and confirm or establish 28 $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption assignments. Four new excited state fundamentals are located: $\nu_4' = 365$ cm^{-1}, $\nu_5' = 749$ cm^{-1}, ν_9' 1148 cm^{-1}, and $\nu_{17}' = 712$ cm^{-1}. A set of 12 vibrations encompassing six of the the ten symmetry species initiates most of the structure in the $^1B_{2u}$–$^1A_{1g}$ transition. Each vibration in these six species is "active".

Fluorescence spectra from a representative set of single vibronic levels (SVL) in the $^1B_{2u}$ state of benzene vapor have been analyzed in the preceding report.[3] Each spectrum was obtained by pumping an absorption band with a well established assignment so that the fluorescence analyses were based on secure knowledge of the emitting levels. Every spectrum followed a consistent pattern of vibronic activity which matched that seen in absorption. In this paper,

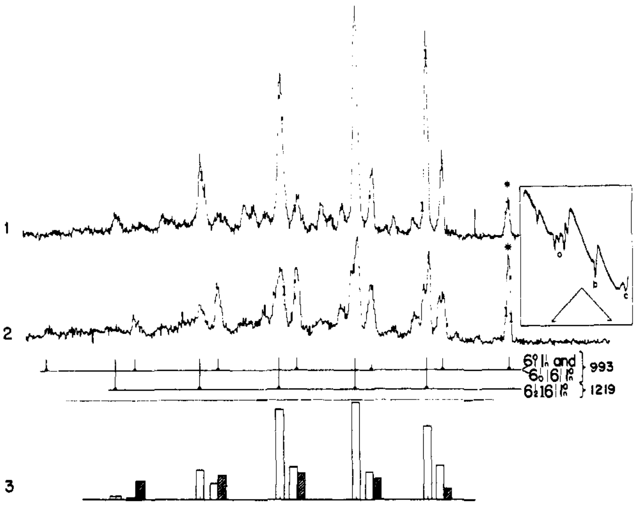

Figure 1. Analysis of a fluorescence spectrum from multiple levels by comparison with fluorescence from a single level. (1) Fluorescence from the state $6^1 16^1$ (taken from part I). (2) Fluorescence from the states 1^1, $6^1 16^1$, and $6^2 16^1$ after excitation into the $6^0_1 1^1_0(B^0_1)$ absorption band (maximum b in the absorption insert). The absorption $6^1_0 16^1_1(A^1_0)$ is at c and absorption $6^2_1 16^1_1(C^1_0)$ is near a. Fluorescence band intensities from $6^2 16^1$ should be similar to those from $6^1 16^1$ emission shown in (1). (3) Assessment of the fluorescence contributions in the lower spectrum to the various emitting levels. The intensity ratios of $6^1_0 16^1_1 1^0_n{:}6^1_2 16^1_1 1^0_{n-1}$ emission from the top spectrum are used to estimate the intensity expected at n993 cm^{-1} in the bottom spectrum due to the states $6^1 16^1$ and $6^2 16^1$. The excess intensity at n993 cm^{-1} must be due to emission from 1^1. The open bar graph shows the normalized combined intensities due to the states $6^1 16^1$ and $6^2 16^1$ and the shaded bar graph shows the emission from 1^1. The projected relative intensities of the progression members in each case approximately match the expected Franck-Condon envelopes. For the B^0_1 spectrum the excitation is centered at 38385 cm^{-1} with a bandpass of 45 cm^{-1}. The fluorescence bandpass is 35 cm^{-1}. The spectra are linear in wavelength. Absorption bands: a, region $C^1_0(6^2_1 16^1_1)$; b, 38,406 cm^{-1} ($B^0_1{:}6^0_1 1^1_0$); c, 38,452 cm^{-1} ($A^1_0{:}6^1_0 16^1_1$).

we extend these fluorescence studies to comment on less certain absorption assignments and to characterize emission from levels with excitation in vibrations additional to the modes ν_1, ν_6, and ν_{16}.

The fluorescence assignments in part I together with previous absorption analyses[4-9] suggested that modes in six of the ten symmetry classes of benzene are active in the $^1B_{2u}$–$^1A_{1g}$ transition. Accordingly, absorptions have been sought which reach levels containing excitation in these modes. The emitting levels are recognized by an SVL fluorescence analysis which is based on the pattern of vibrational activity established in part I.

The spectra in this paper generally originate from levels reached by pumping weak bands lying in crowded absorption regions. Hence conflicting requirements are placed on the excitation. It must be sufficiently intense to pump weak absorption but simultaneously its bandwidth must be narrow enough to bias a single absorption band in a crowded spectrum. Thus some of the following fluorescence spectra have been obtained with excitation bandpasses too broad to pump a single absorption band, and one must loosen the definition of SVL fluorescence in applying the term to these spectra. However, tuned excitation has succeeded in selecting upper state distributions with populations sufficiently biased so that the principal fluorescence transitions from a desired level can be readily seen.

Table I. Strong Progressions Expected in Fluorescence after Pumping the B^0_1 Absorption Region

Emitting level	Fluorescence progressions	Displacement for n = 0, 1, 2, . . .
1^1	$6^1_0 1^1_n$	
$6^1 16^1$	$6^1_0 16^1_1 1^0_n$	0, 993, 1986, . . .
$6^2 16^1$	$6^2_1 16^1_1 1^0_n$	
$6^1 16^1$	$6^1_2 16^1_1 1^0_n$	1219, 2212, 3205, . . .
$6^2 16^1$	$6^2_3 16^1_1 1^0_n$	

Before discussing the individual spectra, it is useful to set forth the simple expectations of fluorescence structure which derive from past absorption assignments and from the SVL fluorescence spectra described in part I. (1) If ν_6 is among the modes excited in an emitting state such as $6^iX^aY^b$, the dominant fluorescence structure is expected to be the *pair* of progressions $6^i_{i+1}X^a_aY^b_b1^0_n$, $6^i_{i-1}X^a_aY^b_b1^0_n$. (2) If the excited state does not contain quanta of ν_6, then a single progression $6^0_1X^a_aY^b_b1^0_n$ will dominate fluorescence.

An exception to these would occur only if a transition with intensity comparable to $\Delta v_6 = \pm 1$ transitions could be induced by other vibrational changes, or if the vibrational overlap integral $\langle X^a | X_{a\pm 2}\rangle$ was large. Neither of these exceptions are known from existing absorption assignments, and neither have been recognized in any of the fluorescence spectra described in part I.

Experimental Section

Experimental details with comments on the presentation of fluorescence spectra and notation have been given in part I. They apply equally to this work with one exception. To enable some of the weaker transitions to be studied with adequate fluorescence resolution, improvements were made to the existing apparatus to boost detection sensitivity. These modifications included changes in the optics used to focus excitation into the fluorescence cell and in the optics used for the collection of fluorescence. The 1.7-m Czerny-Turner scanning spectrometer was fitted with a stepper motor drive system which enables slow and accurate scanning when long counting periods were required because of low fluorescence intensity. A more sensitive photomultiplier (EMI 9789QA) was incorporated in a housing shielded from stray rf signals. Together, these modifications yielded at least an order of magnitude improvement in detection sensitivity and in signal-to-noise ratio. With the exception of Figure 1, spectra are linear in wave number.

Fluorescence Spectra

The following sections describe fluorescence after narrow-band excitation into 12 regions in the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption spectrum. Several new absorption assignments are confirmed. A table containing all absorption assignments established from SVL fluorescence spectra is given in the summary at the conclusion of this discussion.

1^1 Emission After $6^0_1 1^1_0(B^0_1)$ Absorption. The B^0_n absorption bands leading to selective excitation of ν_1' typify the conditions encountered in studies of the weaker absorption bands. Figure 1 shows that the $6^0_1 1^1_0(B^0_1)$ band (absorption maximum b) lies within the rotational envelope of the much stronger absorption $6^1_0 16^1_1(A^1_0)$ at c. Since the latter is essentially a continuum of congestion, it is unlikely that any light source, however monochromatic, could pump the state 1^1 without also pumping $6^1 16^1$.

Fluorescence after pumping the B^0_1 region with excitation overlapping not only the $6^1_0 16^1_1$ band but also the neighboring $6^2_1 16^1_1$ absorption maxima near "a" is shown in Figure 1. The fluorescence is a superposition of emissions from three states 1^1, $6^1 16^1$, and $6^2 16^1$, and it is an instructive excercise to untangle the principal structure of 1^1 fluorescence.

The expected displacements of the dominant progressions from each state are summarized in Table I. It is seen that the emissions from these states are coincident at low resolution so that only two dominant progressions will appear. Such is the case in Figure 1 and, for convenience, these will be called the 993- and the 1219-cm^{-1} progressions.

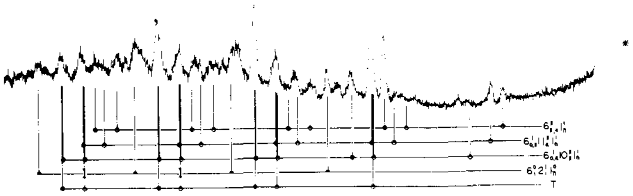

Figure 2. Fluorescence produced by excitation in the region near T_{00} + 2520 cm^{-1}. The spectrum is linear in wave number. The progression $6^0_12^1_11^0_n$ with origin at −3070 cm^{-1} characterizes emission from 2^1. Excitation is centered at 40,603 cm^{-1} with a bandpass of 60 cm^{-1}. Fluorescence bandpass is 25 cm^{-1}. Absorption in this region was too weak to provide sufficient contrast for photoelectric measurement with our apparatus. Maxima and relative intensities in this region taken from Atkinson's compilation[9] are: 40,704.2 cm^{-1} (335) and 40,686.1 cm^{-1} (170) (0^0_1:$6^1_010^2_01^1_0$); 40,648.8 cm^{-1} (18); 40,636.3 cm^{-1} (25); 40,616.8 cm^{-1} (25); 40,603.6 cm^{-1} (25); 40,558.8 cm^{-1} (250) (K^0_1:$6^1_011^2_01^1_0$).

Spectra comparing emission from states 6^1, 6^2, and 6^116^1 (part I) indicated that 6^116^1 and 6^216^1 emissions should be qualitatively similar. Thus it is proper to treat these emissions together as being from a single state, say 6^116^1. Their contributions can then be judged from the 6^116^1 spectrum aligned for reference above the B^0_1 spectrum in Figure 1. By comparing these spectra, it is apparent that additional intensity is supplied to the 993-cm^{-1} progression in the B^0_1 spectrum, and this is the emission from the state 1^1.

The relative intensities of the 993- and 1219-cm^{-1} progressions in 6^116^1 and 6^216^1 emission are known from the upper spectrum in Figure 8, part I, and they can be used to estimate how much of the 993-cm^{-1} progression in the B^0_1 spectrum comes from those levels. The residual intensity in the 993-cm^{-1} progression is 1^1 emission. The dissection is shown in the bar graph of intensities below the B^0_1 spectrum. The 1^1 intensity emerges as it should with the characteristic profile of a progression from an upper level with $\upsilon_1' = 1$. (The strong $\ldots 1^1_0$ member is obscured at the exciting position but the low $\ldots 1^1_1$ intensity and the rise to a second maximum at $\ldots 1^1_3$ are unmistakable. It is this maximum at large *n*, where the $\ldots 1^0_n$ progressions from other levels become weak, which inverts the 993- and 1219-cm^{-1} progression intensities at large displacements.) In total, the 1^1 emission accounts for about 35% of the intensity in the 993-cm^{-1} progression.

2^1 Emission after $6^0_12^1_0$ Absorption. Of the two totally symmetric fundamentals of benzene, ν_1 is substantially more active in forming intense progressions built on false origins. In fact, ν_2 (C–H stretch, $\nu_2'' = 3073$ cm^{-1}) does not play an important role in the absorption spectrum and transitions involving ν_2'' are also difficult to observe in fluorescence. For example, in zero-point fluorescence (see part I), the transition $6^0_12^0_1$ (−3073 cm^{-1}) would be the most intense progression origin involving ν_2''. The transition $10^0_21^0_2$ at −3070 cm^{-1} is nearly coincident and no obvious increase in intensity over that expected from Franck–Condon considerations for the $10^0_21^0_n$ progression is observed at this displacement. Moreover, $6^0_12^0_11^0_1$ would be expected to be a factor of ~1.3 stronger than $6^0_12^0_1$ while $10^0_21^0_3$ would be considerably weaker than its preceding progression member, yet there is no additional intensity at the displacement corresponding to $10^0_21^0_3$.

The S^0_0 absorption band at 41,741.4 cm^{-1} [6,9] was assigned[6] as $6^1_02^1_0$. Our attempts to excite fluorescence by pumping S^0_0 have not proven successful. Not only is S^0_0 absorption relatively weak, but the level 6^12^1 lies well above the previously established "threshold" for observation of fluorescence from benzene vapor.[10]

The hot band $6^0_12^1_0$ offers an alternative opportunity to see emission from a state containing excitation in ν_2. Although weaker than S^0_0 due to the Boltzmann factor, $6^0_12^1_0$ lies below the threshold and indeed, Figure 2 indicates that we have been successful in observing 2^1 emission. Excitation has been tuned to the predicted $6^0_12^1_0$ region (assuming $\nu_2' = 3130$ cm^{-1}, as derived from S^0_0), but due to the overwhelming intensity of neighboring absorption, the stronger fluorescence structure does not originate from 2^1. The bulk of assigned absorption transitions in this region are to levels with at least one quantum of ν_1'.[9] In Figure 2, progression markers show emission from the levels $6^111^21^1$, 6^31^1 (after $6^3_01^1_0$ excitation; see K^0_0 emission below), and $6^110^21^1$. Each reflects the characteristic Franck–Condon envelope for a $\upsilon_1' = 1$ progression. In contrast, the progression matching the expected displacements of $6^0_12^1_11^0_n$ has a Franck–Condon envelope consistent with $\upsilon_1' = 0$. The progression origin (−3070 cm^{-1} observed) appears at the correct position (−3073 cm^{-1} calculated).

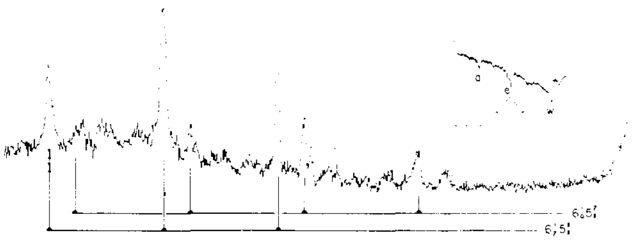

Figure 3. Fluorescence from the state 6^15^2. Spectra are linear in wave number. The dominant emission occurs as the progressions $6^1_{0,2}5^2_2$. Excitation is centered at 40,108 cm^{-1} with a bandpass of 20 cm^{-1}; fluorescence bandpass is 25 cm^{-1}. Absorption bands: a, 40,090.8 cm^{-1} (B^1_3:$6^0_116^1_11^3_0$); e, 40,108.9 cm^{-1} ($6^1_05^2_0$); w, 40,131.9 (A^2_2:$6^1_016^2_21^2_0$).

Further evidence for the assignment is given by the observation that $6^0_12^1_1$ rather than $6^0_12^1_0$ is the dominant fluorescence transition from 2^1. This is consistent with the general absence of ν_2 progressions from fluorescence and absorption. Both fulfill the expectation that the Franck–Condon integrals $\langle \phi_2'(n)|\phi_2''(m)\rangle$ are small for $n \neq m$ because of a small coordinate displacement, ΔQ_2, upon electronic excitation.

Thus, although the evidence is by no means unambiguous, it suggests that $6^0_12^1_0$ does lie in this absorption region, it may be the band so assigned by Atkinson[9] at 40,603.6 cm^{-1} giving $\nu_2' = 3122$ cm^{-1} or the band at 40,616.8 cm^{-1} giving $\nu_2' = 3135$ cm^{-1}. ν_2' derived from S^0_0 is 3130 cm^{-1}.

A strong progression labeled T in Figure 2 has not been assigned. The intensity profile is suggestive of an upper state with $\upsilon_1' = 2$ and $\upsilon_6' \geq 1$. The origin for the $\Delta\upsilon_6 = -1$ progression underlies $6^1_211^2_21^1_0$ at a displacement of ~2600 cm^{-1}.

Emission from 6^15^2 after $6^1_05^2_0$ Absorption. Whereas ν_4 (b_{2g}) is known both in absorption (see below) and emission,[3] activity in the other b_{2g} mode of benzene, ν_5, has not held a sustained assignment. (An early absorption assignment[6] has been shown by Atkinson[9] to be incorrect.) An unassigned absorption band, thought by Atkinson[9] to be a progression origin, was probed with tuned excitation in an attempt to identify the transition. Figure 3 shows the spectrum obtained after selective excitation of this absorption band at 40,108.9 cm^{-1}. Although absorption in this region is congested, the fluorescence spectrum is dominated by two progressions, readily identified as $\Delta\upsilon_6 = \pm 1$ transitions, with progression origins at −1982 and −3202 cm^{-1}. The former displacement corresponds almost exactly to $2\nu_5''$ (calculated −1980 cm^{-1}) while the latter is clearly $2\nu_5'' + 2\nu_6''$.

Absorption e in Figure 3 is thus assigned as $6^1_05^2_0$ where ν_5 is Franck–Condon active only. Assuming no anharmonic contributions, the frequency for ν_5 in the $^1B_{2u}$ state is derived as 749 cm^{-1}.

Figure 4. Fluorescence from 7^1 after $7^1_0(Q^0_0)$ excitation. Both absorption and fluorescence spectra are linear in wave number. The strongest emission is seen as the progression $6^0_1 7^1_1 1^0_n$. Excitation is centered at 41,156 cm^{-1} with 52 cm^{-1} bandpass; fluorescence bandpass is 16 cm^{-1}. Absorption bands: r, 41,125.5 cm^{-1}; s, 41,128.3 cm^{-1}; $7^1_0(Q^0_0)$, 41,165.3 cm^{-1}; t, 41,168.4 cm^{-1}; u, 41,173.5 cm^{-1}.

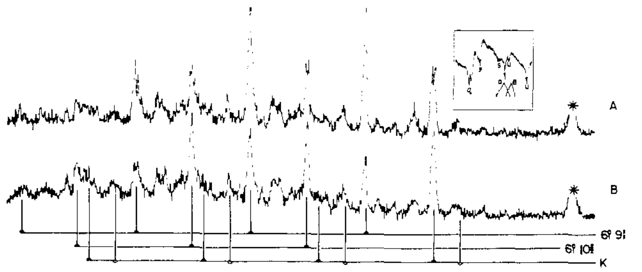

Figure 5. Fluorescence from the states 9^1 and 10^2. Both absorption and fluorescence spectra are linear in wave number. In spectrum A, the progression $6^0_1 9^1_1 1^0_n$ is dominant. Excitation has been tuned to maximize absorption in the transition whose band maximum is marked t. In spectrum B, excitation has been moved away from t toward v and the result is to enhance the intensity of the progression $6^0_1 10^2_2 1^0_n$ while $6^0_1 9^1_1 1^0_n$ diminishes. A third progression marked K contains both $\Delta v_6 = +1$ and $\Delta v_6 = -1$ transitions, shown on the same line as closed and open semicircles, respectively. Spectrum A: excitation is centered at 39,235 cm^{-1} with 12 cm^{-1} bandpass; fluorescence bandpass is 13 cm^{-1}. Spectrum B: excitation is centered at 39,238 cm^{-1} with 8 cm^{-1} bandpass; the fluorescence bandpass is 19 cm^{-1}. Absorption bands: q, 39,206.3 cm^{-1}; r, 39,215.7 cm^{-1}; s, 39,231.3 cm^{-1}; t, 39,235.8 cm^{-1} (9^1_0); u, 39,239.0 cm^{-1}; v, 39,255.0 cm^{-1} (10^2_0).

By way of corollary, the previously unidentified absorption band at 39,422.8 cm^{-1} is assigned as the second-order Herzberg–Teller transition, $5^1_0 10^1_0$. This can be seen as follows. The known transition $4^0_1 10^1_0$ is analogous and has a maximum-origin separation[8] of ~2 cm^{-1}. This places the $5^1_0 10^1_0$ band *origin* at 39,420.8 cm^{-1}. Hence

$$\begin{aligned} 39{,}420.8\ \mathrm{cm}^{-1} &= 38{,}086.1\ \mathrm{cm}^{-1}(\mathrm{T}_{00}) + 1334.7\ \mathrm{cm}^{-1} \\ &= \mathrm{T}_{00} + 585\ \mathrm{cm}^{-1} + 749.7\ \mathrm{cm}^{-1} \\ &= \mathrm{T}_{00} + \nu_{10}' + \nu_5' \end{aligned}$$

Congestion hides the analogous transition, $5^0_1 10^0_1$, in zero-point fluorescence.[3] Similarly, the transition $6^0_1 5^0_2$ would lie in a region overlapped by strong fluorescence and cannot be discerned from other structure. However, higher resolution studies of $6^1 1^1$ fluorescence[11] suggest that $6^1_1 5^0_1 10^0_1 1^1_0$ is present with appropriate intensity.

7^1 Emission after $7^1_0(Q^0_0)$ Absorption. The Q^0_0 absorption band at 0,0 + 3077 cm^{-1} was assigned originally[4] as $6^1_0 2^1_0$. However, the rotational analysis of Callomon, Dunn, and Mills[8] shows, in agreement with Garforth and Ingold,[6] that 7^1_0 is the preferred assignment. The fluorescence spectrum obtained by pumping Q^0_0 (Figure 4) offers confirmation. The dominant intensity appears as the progression $6^0_1 7^1_1 1^0_n$, whose first member lies at a displacement of −3668 cm^{-1} (cf. −3664 calculated). The Franck–Condon envelope is consistent with a $v_1' = 0$ upper state.

Additional structure, not attributable to emission from 7^1, is marked as the progressions L and A. The progression origins occur at displacements −2636 and −3853 cm^{-1}, corresponding to $\Delta v_6 = -1$ and $\Delta v_6 = +1$ transitions, respectively. The intensity distribution among progression members is indicative of an upper state for which $v_1' = 0$, but further identification has not been pursued. The assignments proposed[6] for the absorption bands marked t and u in Figure 4, namely $11^1_0 17^1_0 1^2_0$ and $6^0_1 1^4_0$, respectively, offer no comfort since neither transition would lead to the observed fluorescence structure.

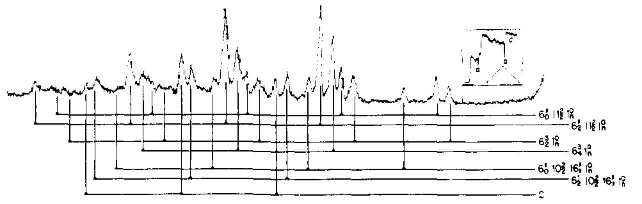

Figure 6. Fluorescence from $6^1 11^2$ excited by pumping absorption $6^1_0 11^2_0(K^0_0)$. Emission from other states is also present. The fluorescence spectrum is linear in wave number. Fluorescence bandpass is 28 cm^{-1}. Excitation is centered at 39,633 cm^{-1} with a 56 cm^{-1} bandpass. Absorption bands: a, 39,561 cm^{-1}; b, 39,638 cm^{-1} (K^0_0); c, 39,656 cm^{-1}.

Observation of fluorescence from 7^1 is of further interest since it is so far the highest level above the $^1B_{2u}$ origin from which fluorescence has been characterized. Callomon, Parkin, and Lopez-Delgado[10] have observed that many of the absorption bands involving vibrational levels more than 3000 cm^{-1} above the $^1B_{2u}$ zero-point level are diffuse, implying fast nonradiative decay.[12] The absorption 7^1_0 is an exception. It is sharp and moreover its two higher progression members, $7^1_0 1^{1,2}_0(Q^0_1,Q^0_2)$, also show no detectable line broadening. The fluorescence quantum yield of 7^1 is, however, considerably less than yields measured for lower levels. By comparison with fluorescence from 6^1, whose quantum yield[13] is 0.27, we find $\phi_f \approx 0.04$ for 7^1. This corresponds to a decay time of about 18 nsec which fits an estimate by Spears and Rice.[14]

9^1 Emission After 9^1_0 Absorption. The identification of ν_9' emerges most convincingly from the fluorescence spectra shown in Figure 5. Excitation tuned to maximize absorption in the transition t results in an emission spectrum (A) whose dominant structure is the progression $6^0_1 9^1_1 1^0_n$ with origin at a displacement of −1787 cm^{-1} (cf. −1786 calculated). Strong emission from 10^2 is apparent also as the progression $6^0_1 10^2_2 1^0_n$. As excitation is moved away from t towards v, the intensity of emission from 10^2 increases while that from 9^1 decreases (spectrum B). The progressions labeled K must arise as a result of excitation to some other level since the Franck–Condon envelope has the unmistakable character of emission from a $v_1' = 1$ upper state.

These spectra support assignment of the absorption band t (39,235.8 cm^{-1}) as 9^1_0. The band is best described as having a type *II* rotational contour[8] for which the maximum-origin separation is in the vicinity of 2 cm^{-1}, whence $\nu_9' =$ 1148 cm^{-1}.

$6^1 11^2$ Emission after $6^1_0 11^2_0(K^0_0)$ Absorption. The K^0_0 band shown as absorption maximum b in Figure 6 is assigned as the absorption progression origin $6^1_0 11^2_0$. The SVL fluorescence spectrum is consistent with this assignment. The strongest fluorescence progression matches the positions and Franck–Condon envelope of the dominant structure expected from $6^1 11^2$, namely the progression $6^1_2 11^2_2 1^0_n$. Furthermore the weaker $\Delta v_6 = -1$ progression $6^1_0 11^2_2 1^0_n$ also appears in fluorescence with the proper relative intensity.

The five additional progressions prominent in Figure 6 probably arise from other excited states. The sequence absorption band $6^1_0 10^2_0 16^1_1$ must lie near 39,622 cm^{-1} which is just 11 cm^{-1} from the excitation maximum. Two fluorescence progressions can be identified from this absorption. They are the expected $\Delta v_6 = \pm 1$ fluorescence progressions displaying the correct displacements, the appropriate Franck–Condon intensity profiles, and the correct intensity relationships to each other.

The strongest progressions not attributable to $6^1 11^2$ sup-

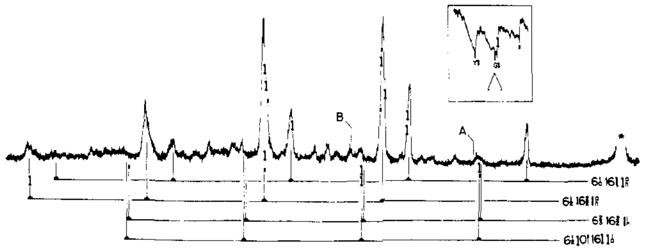

Figure 7. Fluorescence generated by pumping the G^0_0 absorption band group. The most prominent fluorescence progressions are from the level $6^1 16^2$ excited by the absorption $6^1_0 16^2_0$. Fluorescence bandpass is 15 cm^{-1}. Excitation is centered at 39,080 cm^{-1} with a 28 cm^{-1} bandpass. Absorption bands: Y^0_0, 39,038.5 cm^{-1}; G^0_0 39,082.1 and 39,087.5 cm^{-1}; t, 39,134 cm^{-1}.

port an absorption assignment 6^3_0 suggested to us by Atkinson.[9] This absorption is symmetry allowed but weak (third-order Herzberg–Teller) with a calculated position 39,655 cm^{-1} near bands just to higher energy from the K^0_0 maximum. It should have only one observable angular momentum component $6^3_0 l^1_0$. The emission progressions $6^3_4 1^0_n$ and $6^3_2 1^0_n$ are expected to dominate 6^3 fluorescence with relative intensities roughly 2:1 and both should have $v_1' = 0$ progression profiles. The markers on Figure 6 show the calculated displacements 2438 and 1219 cm^{-1} for the progression origins. Both the band positions and intensity relationships are consistent with the expectations.

The fluorescence progression marked C whose origin is near 2990 cm^{-1} from the excitation maximum is clearly emission from an upper state with $v_1' = 0$, but it remains unassigned.

$6^1 16^2$ Emission after $6^1_0 16^2_0(G^0_0)$ Absorption. A level with $\nu_{16}' = 2$ can be reached via the G^0_0 absorption bands which have long held the assignment $6^1_0 16^2_0$.[4,6] Figure 7 shows this absorption region and the fluorescence produced by selective excitation of the G^0_0 band group.

The excitation pumps several absorption transitions which lie near the two prominent band maxima in the G^0_0 group. However, emission from the level $6^1 16^2$ is dominant among the fluorescence structure. As expected, the strongest progressions are $6^1_0 16^2_2 1^0_n$ and $6^1_2 16^2_2 1^0_n$. Their relative intensities and Franck–Condon envelopes are wholly consistent with these assignments.

All other $6^1 16^2$ fluorescence transitions are weak. While they contribute to some of the minor structure, there are many other weak bands present in the spectrum which cannot be accounted for in terms of $6^1 16^2$ fluorescence. Some of the latter can be readily identified as emisssion from other fluorescing levels.

Assignments in other absorption regions suggest five absorption bands which may lie in the region spanned by excitation.

$10^2_0 16^1_1$	$9^1_0 16^1_1$
$6^1_0 10^1_1 16^1_1 1^1_0$	$6^1_0 16^3_3 1^1_0$
$6^2_1 16^2_2 1^1_0$	

It is by no means clear that all would be sufficiently intense to be among the distinct absorption structure. Emission can be recognized only from the three levels reached by absorptions in the left column.

Markers showing calculated positions for the dominant fluorescence progressions from the emitting levels $6^2 16^2 1^1$ and $6^1 10^1 16^1 1^1$ each coincide with observed structure. These progressions have $\Delta v_6 = +1$ origins 1219 cm^{-1} from their respective absorption maxima. The absorption maxima, $6^2_1 16^2_2 1^1_0$ (39,115 cm^{-1}) and $6^1_0 10^1_1 16^1_1 1^1_0$ (39,100 cm^{-1}), are separated by 15 cm^{-1} so that their fluorescence progressions would also be separated by 15 cm^{-1}. The dominant progression from the latter, $6^1_2 10^1_1 16^1_1 1^1_n$, appears stronger as expected since the excitation is centered nearer $6^1_0 10^1_1 16^1_1 1^1_0$. The observed progression intensities lie intermediate to those expected for either $v_1' = 0$ or $v_1' = 1$ progressions. Since there is no reason to believe that either emission is absent, this suggests that a third progression from an unidentified state with $v_1' = 0$ underlies that region.

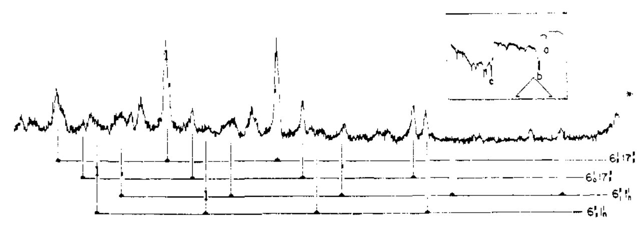

Figure 8. Fluorescence from $6^1 17^2$ excited by pumping the $6^1_0 17^2_0(B'^0_0)$ absorption band (maximum d). The component 1^0_n must be added to the assignments $6^1_{0,2} 17^2_2$. The fluorescence spectrum is linear in wave number. Excitation is centered at 40,045 cm^{-1} with a 28 cm^{-1} bandpass. Absorption bands: a, 40,056.4 cm^{-1}; b, 40,050.2 cm^{-1} (B'^0_0:$6^1_0 17^2_0$); c, 40,010.0 cm^{-1}.

Emission after the absorption $9^1_0 16^1_1$ should appear in a progression $6^0_1 9^1_1 16^1_1 1^0_n$ beginning at about −1785 cm^{-1} from excitation. This nearly coincides with the strong band $6^1_0 16^2_2 1^0_1$ from the dominant emitting state. There is no obvious burst of intensity in that band; at best, emission from the state $9^1 16^1$ must be weak.

Emission from excitation of the A^3_1 absorption band (which lies in the deep absorption minimum between Y^0_0 and G^0_0 in Figure 7) cannot be observed. Its strongest fluorescence band ($6^1_2 16^3_3 1^1_0$) would be at the position marked A on Figure 7.

Position B in Figure 7 shows the expected position of the strongest emission band from $10^2 16^1$ after absorption $10^2_0 16^1_1$. A band is found there but there is no accompanying evidence in support of such an assignment.

We have been unable to find an assignment for the strong emission band seen about 200 cm^{-1} toward lower energy from position B.

$6^1 17^2$ Emission after $6^1_0 17^2_0(B'^0_0)$ Absorption. One of the more successful attempts to probe an absorption assignment and to obtain fluorescence from a level with excitation in modes other than ν_1, ν_6, and ν_{16} has followed pumping the absorption labeled B'^0_0 by Radle and Beck.[7] The original absorption assignment[4] $6^0_1 2^1_0$ is known to be incorrect since the corresponding cold absorption band $6^1_0 2^1_0$, with this choice for ν_2', is absent. Furthermore, evidence presented above suggests that $6^0_1 2^1_0$ lies elsewhere in the absorption spectrum. A later assignment of the B'^0_0 band by Garforth and Ingold[6] as $6^2_0 1^1_0$ (their U^0_1 band) has been rejected on the basis of both position and rotational contour.[8] Finally Atkinson[9] has proposed the assignment $6^1_0 17^2_0$. The SVL fluorescence spectrum is consistent with the latter suggestion but is indicative that $6^2_0 1^1_0$ must also lie in this region of absorption.

The B'^0_0 band (b in Figure 8) lies in a crowded absorption region so that fluorescence is congested. However, four prominent progressions emerge and the most intense correspond to the progressions $6^1_2 17^2_2 1^0_n$ and $6^1_0 17^2_2 1^0_n$ expected to dominate fluorescence from $6^1 17^2$. The $\Delta v_6 = +1$ progression intensity properly exceeds that of the $\Delta v_6 = -1$ progression by a factor of 2–3 and the Franck–Condon envelopes are clearly those of emission from a state with $v_1' = 0$. The transitions $6^1_{0,2} 17^2_0$ and $6^1_{0,2} 17^2_4$ contribute little intensity to the fluorescence spectrum, and this is consistent with the expectation that Δv_x will be zero in modes other than ν_1 and ν_6 for *strong* transitions.

The remaining strong fluorescence appears as two progressions whose origins lie near −608 cm^{-1} ($\Delta v_6 = -1$) and −1830 cm^{-1} ($\Delta v_6 = +1$). In no other fluorescence spec-

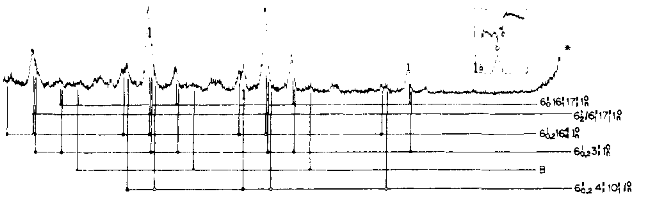

Figure 9. Fluorescence produced by pumping the band group E_0^0 (the region near b and c in the absorption insert). Numerous absorption transitions are expected to be excited. The assignment markers for $6_{0,2}^1 16_4^4$ and $6_{0,2}^1 3_1^1$ include on the same line both the $\Delta v_6 = +1$ and $\Delta v_6 = -1$ progressions (closed and open circles, respectively). Marker B is calculated for an origin displaced 2207 cm^{-1} from absorption maximum b. The fluorescence spectrum is linear in wave number. The excitation bandpass is 16 cm^{-1} and the fluorescence bandpass is 19 cm^{-1}. Excitation is centered at 39,560 cm^{-1}. Absorption bands: a, the higher energy edge of the $6_0^1 1_0^1(A_1^0)$ band; b, 39,560 cm^{-1}; c, 39,568 cm^{-1}.

trum have we observed an origin at -608 cm^{-1}, corresponding to *one* quantum of ν_6'' alone. The $\Delta v_6 = \pm 1$ selection rule demands that the upper state in this instance must be 6^2 and hence the absorption transition can only be $6_0^2 1_0^n$. The unmistakable $v_1' = 1$ Franck–Condon profile for these progressions identifies the upper state as $6^2 1^1$. This result does not contradict the prediction[8] that $6_0^2 1_0^1$ absorption would have a featureless rotational band contour. Such a contour does not preclude moderately strong absorption. The absorption maximum "a" in Figure 8, just 6 cm^{-1} toward higher energy than $6_0^1 17_0^2$, coincides almost exactly with the predicted position for $6_0^2 1_0^1$.

Emission after E_0^0 Absorption. The E_0^0 bands (maxima b, c, and others in that group, Figure 9) have never been assigned satisfactorily. The original assignments[4,6] suggested that the absorption 8_0^1 was responsible for structure in that group, but the rotational analysis[8] indicates that the 8_0^1 band contour would be without a distinct maximum. A recent magnetic circular dichroism study[15] suggests that 8_0^1 absorption may be away from the E_0^0 region and near 39,600 cm^{-1}.

Two facts guide the search for additional absorption assignments. First, the E_0^0 bands are known to be progression origins, and second, it has been shown by Callomon, Christie, and Jordan[16] that the E_0^0 group is comprised dominantly of cold absorption bands. It would be unlikely, for example, that the absorption $6_1^2 1_0^2$ which is calculated to lie near this region could be a strong contributor either to the E_0^0 absorption structure or the fluorescence in Figure 9.

With these criteria and a knowledge of the general pattern of vibrational activity in the $^1B_{2u}$–$^1A_{1g}$ transition, the following possibilities for absorption in the E_0^0 region are considered: (a) $6_0^1 16_0^4$, expected to be a weak transition but it should lie in this region;[8] (b) $6_0^1 16_0^1 17_0^1$, a combination analogous to transitions seen elsewhere (it should occur with moderate intensity in the E_0^0 region);[9] (c) $6_0^1 3_0^1$, Christie[17] has suggested this second-order Herzberg–Teller transition; this would be the only opportunity for ν_3 to appear with significant intensity in absorption; it would establish $\nu_3 \approx 950$ cm^{-1}; (d) $6_0^1 4_0^1 10_0^1$, the analogous second-order transitions, $4_0^1 10_0^1$ and $16_0^1 17_0^1$ are nearly coincident in the Y_0^0 absorption region (see discussion of Y_0^0 emission below). The fluorescence spectrum is dominated by two progressions whose origins show maxima near displacements of 1375 and 2595 cm^{-1} from the excitation maximum. Each of two proposed E_0^0 absorptions would excite a pair of strong fluorescence progressions with origins nominally at these positions.

Absorption $6_0^1 16_0^1 17_0^1$	Absorption $6_0^1 3_0^1$
$6_0^1 16_1^1 17_1^1$ (calcd 1366 cm^{-1})	$6_0^1 3_1^1$ (calcd 1350 cm^{-1})
$6_2^1 16_1^1 17_1^1$ (calcd 2585 cm^{-1})	$6_2^1 3_1^1$ (calcd 2569 cm^{-1})

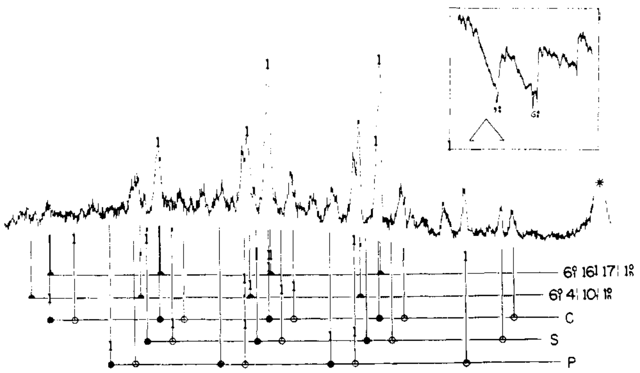

Figure 10. Fluorescence from $4^1 10^1$ and $16^1 17^1$ produced by pumping the Y_0^0 band. The fluorescence spectrum is linear in wave number. Excitation is centered at 39,030 cm^{-1} with a 28 cm^{-1} bandpass. The fluorescence bandpass is 16 cm^{-1}. Absorption maxima are Y_0^0 (39,038.5 cm^{-1}) and G_0^0 (39,082.1 cm^{-1}, 39,087.5 cm^{-1}).

It is safe to assume that the observed fluorescence progressions arise from the absorption whose maximum is at "b", and the progression markers in Figure 9 are calculated upon this premise.

The fluorescence resolution is sufficient to discriminate between the emissions from the two levels since the progression origin bands are narrow and seem free of overlapping transitions. On this basis, the assignment of $6_0^1 16_0^1 17_0^1$ absorption at maximum "b" seems well supported. Each band fits the expectations for $6^1 16^1 17^1$ emission closely whereas the fit to $6^1 3^1$ emission is, at best, unlikely. Further support to the assignment derives from the combined ν_{16}, ν_{17} activity seen elsewhere in absorption. For example, the Y_0^0 absorption region has been shown by SVL fluorescence study to contain the absorption $16_0^1 17_0^1$ (see below), and in fact the Y_0^0 band itself at 38038.6 cm^{-1} seems directly related to the maximum "b" in the E_0^0 regions. Their maxima differ by 522.0 cm^{-1} which is clearly ν_6'. This is consistent with the assignments

$$39560.6(6_0^1 16_0^1 17_0^1(E_0^0)) - 39038.6(16_0^1 17_0^1(Y_0^0)) = \nu_6'$$

No such relationship could be accounted for if the E_0^0 band was assigned $6_0^1 3_0^1$ since the transition 3_0^1 by itself is symmetry forbidden. If one assumes the rotational origin of absorption bands is 3 cm^{-1} below the band maxima,[8] the assignments $6_0^1 16_0^1 17_0^1$ and $16_0^1 17_0^1$ give $\nu_{17}' = 712.5$ and 712.3 cm^{-1}, respectively.

Activity in ν_3 has not been recognized anywhere in fluorescence, but as a fluorescence component . . . 3_1^0 it would be everywhere obscured by the known fluorescence component . . . 1_2^0 because both lead to similar displacements (1350 vs. 1348 cm^{-1}).

Emission from the level $6^1 4^1 10^1$ appears as two progressions, $6_0^1 4_1^1 10_1^1$ and $6_2^1 4_1^1 10_1^1$, with origins at -1553 and -2772 cm^{-1} respectively. The Y_0^0 absorption region has been shown to contain the absorption $4_0^1 10_0^1$ (see below), and an argument analogous to that offered in support of the assignment $6_0^1 16_0^1 17_0^1$ leads one to conclude that the E_0^0 region must also contain the absorption $6_0^1 4_0^1 10_0^1$.

Fluorescence excited by $6_0^1 16_0^4$ absorption appears to be present as marked in Figure 9. Two weak progressions of appropriate relative intensities and Franck–Condon profiles match the calculated positions of the two strong progressions expected from $6^1 16^4$.

The original ν_8 assignment of E_0^0 structure (absorption 8_0^1) predicts an upper level whose emission spectrum would be analogous to that seen from 7^1 and 9^1 (see above) and thus dominated by the single strong progression $6_1^0 8_1^1 1_n^0$. The progression origin will be about 2200 cm^{-1} from the maximum of 8_0^1 excitation when ground state Fermi resonance is

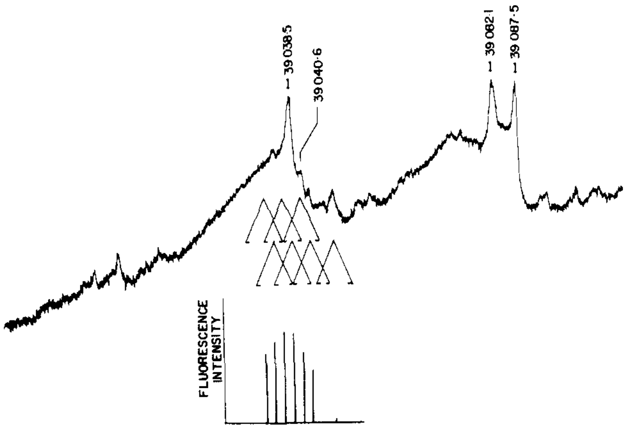

Figure 11. The relative fluorescence intensity of the transition $6_1^0 4_1^1 10_1^1$ as a function of excitation wavelength. The excitation position and profile for each successive measurement of intensity is shown superimposed on the absorption spectrum of the Y_0^0 region. The corresponding fluorescence intensity is represented schematically by the bar graph directly below. In every case, the excitation bandpass was 8 cm^{-1}.

considered. This nearly coincides with a weak $\nu_1' = 0$ progression marked B on the schematic of Figure 9, but except for the fact that this progression is otherwise without assignment, there is no supporting evidence.

$16^1 17^1$ and $4^1 10^1$ Emission after Y_0^0 Absorption. The absorption profile in Figure 10 contains the two prominent G_0^0 and Y_0^0 band groups of Ingold.[6] As discussed earlier, the G_0^0 assignment is secure as $6_0^1 16_0^2$. The Y_0^0 assignment, however, has never been settled. Proposals include $4_0^1 10_0^1$, $16_0^1 17_0^1$, and 9_0^1.[8,6,9] Y_0^0 fluorescence is consistent with the first two but not the last.

The spectrum shown in Figure 10 has been obtained with excitation tuned to excite the Y_0^0 region selectively. As demonstrated above, $\nu_9' = 1148$ cm^{-1} so that 9_0^1 absorption could not occur near the Y_0^0 bands.

The strongest progression in Y_0^0 fluorescence fits precisely the expectations for $16^1 17^1$ emission after $16_0^1 17_0^1$ absorption. It matches the position calculated for the single strong progression form $16^1 17^1$, it has the correct Franck–Condon envelope for a $\upsilon_1' = 0$ progression, and it seems unrelated to other prominent structure in the spectrum. Discussion in the previous section argues that the Y_0^0 maximum at 39,038.6 cm^{-1} is itself $16_0^1 17_0^1$ absorption.

The evidence for $4^1 10^1$ emission after $4_0^1 10_0^1$ absorption is equally convincing. As in the previous case, the most intense progression, $6_1^0 4_1^1 10_1^1 1_n^0$, expected from this level fits a strong progression and has the proper Franck–Condon envelope.

As discussed in part I, the transition $16_1^0 17_1^0$ is exceedingly weak in zero-point fluorescence whereas $4_1^0 10_1^0$ is among the more prominent minor structure. Figure 11 shows the results of an attempt to locate $4_0^1 10_0^1$ absorption more securely. Narrow band excitation has been scanned across the Y_0^0 absorption region and at each position of excitation, the relative intensity of the $6_1^0 4_1^1 10_1^1$ fluorescence transition has been measured. Maximum fluorescence occurs for excitation near the Y_0^0 maximum itself, suggesting that the Y_0^0 maximum corresponds to $4_0^1 10_0^1$. This would be consistent with the evidence from fluorescence that $4_1^0 10_1^0$ is considerably stronger than $16_1^0 17_1^0$ and therefore $16_0^1 17_0^1$ would be expected to be one of the weaker bands near Y_0^0. However, in Figure 10, $16^1 17^1$ fluorescence is *stronger* than $4^1 10^1$ fluorescence. No entirely satisfactory explanation has been found for this apparent inconsistency. However, it is feasible that emission from other levels contributes toward part of the intensity of the $6_1^0 16_1^1 17_1^1 1_n^0$ progression. The progression labeled C with origin at ~790 cm^{-1} may correspond to residual $6^1 16^2$ emission after absorption into the tail of G_0^0.

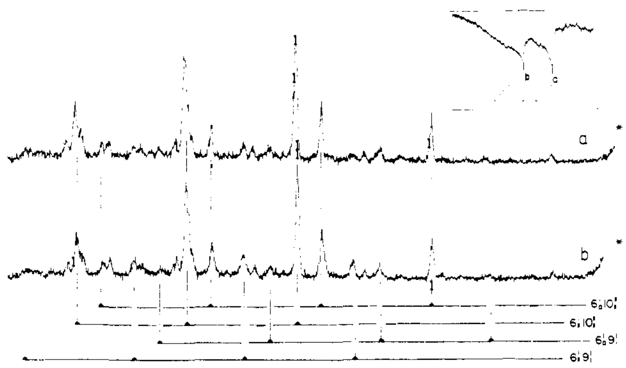

Figure 12. Fluorescence produced by pumping the O_0^0 bands. Upper spectrum: fluorescence after selectively pumping the absorption "a" whose band maximum is at 39,783.1 cm^{-1}. Lower spectrum: fluorescence after pumping the absorption band "b", maximum 39,765.0 cm^{-1}. Both absorption and emission spectra are linear in wave number. (a) Excitation is centered at 39,782 cm^{-1} with a bandpass of 24 cm^{-1}. (b) Excitation is centered at 39,757 cm^{-1} with a 18 cm^{-1} bandpass. The fluorescence bandpass is 15 cm^{-1} in each case.

If this were the case, the $6_2^1 16_2^2 1_n^0$ progression would merge, at our resolution, with $6_1^0 16_1^1 17_1^1 1_n^0$. Taking Y_0^0 to be $4_0^1 10_0^1$ and assuming a maximum-origin separation[8] of ~2 cm^{-1}, we derive the result $\nu_4' \sim 365$ cm^{-1}.

The origin of progression P coincides with that of the expected progression $6_2^1 16_3^3 1_n^1$ after exciting the nearby A_1^3 absorption, $6_0^1 16_3^3 1_0^1$. However, the intensity profile is not appropriate for a $\upsilon_1' = 1$ progression. The transition 16_0^4 is calculated to lie very close to the excitation maximum shown in Figure 10. The strongest fluorescence from 16^4 would be the $\upsilon_1' = 0$ progression $6_1^0 16_4^4 1_n^0$ whose origin (-2204 cm^{-1}) coincides roughly with the weak 1_1^1 member of $6_2^1 16_3^3 1_n^1$. This satisfactorily explains the incorrect intensity profile observed for A_1^3 emission. Evidence from zero-point fluorescence[3] supports the validity of the assignment 16_0^4.

The progression labeled S (origin -890 cm^{-1}) most likely originates from an upper state with $\upsilon_1' = 1$ but no assignment has been found.

Emission after O_0^0 Absorption. The pair of bands a and b in Figure 12 comprise the absorption region labeled O_0^0 (letter O; not to be confused with a 0,0 transition) by Garforth and Ingold[6] who assigned these bands as $6_0^1 10_0^2$. They represent an opportunity to excite molecules with activity in ν_{10} but a complication arises. Callomon, Dunn, and Mills have shown that only one of these bands can be $6_0^1 10_0^2$, and that furthermore, both bands are perturbed by an interaction between their terminating levels.[8]

The fluorescence spectra in Figure 12 have been obtained with excitation tuned to maximize selective pumping of the transitions a (upper spectrum) and b (lower spectrum). The spectra are aligned so that displacements of fluorescence bands from their respective absorption maxima, a or b, can be compared. It is readily apparent that excitation of either "a" or "b" gives rise to almost identical spectra. Measurements of fluorescence band positions at higher resolution show displacements from the respective absorption maxima which are identical within the ±2 cm^{-1} accuracy of our measurements. The two prominent progressions seen in both spectra in Figure 12 are thus labeled $6_{0,2}^1 10_2^2$ where the upper state in each case carries the signature of the state $6^1 10^2$, although one lies ~18 cm^{-1} higher in energy.

In a previous report,[18] it was suggested that the higher energy absorption was $6_0^1 10_0^2$ whereas band "b" was the absorption $6_0^1 9_0^1$. That analysis, which now requires revision, relied on lower resolution spectra. The fluorescence in Figure 12 shows that structure attributable to $6^1 9^1$ is always relatively weak; it does not become prominent when band

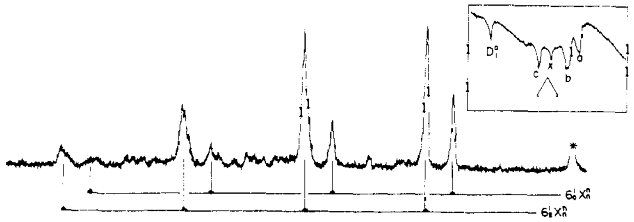

Figure 13. Fluorescence produced by exciting the absorption band at T_{00} + 264 cm^{-1}. Both fluorescence and absorption are linear in wave number. Excitation is centered at 38,349 cm^{-1} with a 12 cm^{-1} bandpass. The fluorescence bandpass is 15 cm^{-1}. Absorption bands: a, 38,366.3 cm^{-1}, 38,364.7 cm^{-1}; b, 38,359.7 cm^{-1}, 38,354.4 cm^{-1}; both a and b are assigned as components of C^1_0:$6^2_1 16^1_1$; x, 38,350.2 cm^{-1}; c, 38,343.3 cm^{-1} (M^0_0:$6^1_0 10^1_1$); d, 38,316.8 cm^{-1} (D^0_1:$6^1_2 1^1_0$).

"b" is pumped (lower spectrum). The transition $6^1_0 9^1_0$ must lie in this region since ν_9' has been established as 1148 cm^{-1} (see above), but it is not responsible for strong absorption. This conclusion is not surprising since although both the first-order transitions, 7^1_0 and 9^1_0, are reasonably strong, no band of comparable intensity is found near the calculated position for $6^1_0 7^1_0$, and one would therefore not expect a priori that the analogous second-order transition $6^1_0 9^1_0$ was strong.

The O^0_0 bands both seem induced by the absorption $6^1_0 10^2_0$. However, the existence of a pair of bands is not readily explained in terms of a Fermi resonance between $6^1 10^2$ and another level. If, for example, a level X^n was nearly degenerate with the unperturbed level $6^1 10^2$, Fermi resonance would cause the upper states to have mixed character and excitation into either "a" or "b" would produce appropriate proportions of X^n fluorescence and $6^1 10^2$ fluorescence, depending on the mixing coefficients. Experience suggests that the strongest fluorescence from X^n would manifest itself as the single progression, $6^0_1 X^n_n 1^0_n$. Since the O^0_0 bands are of similar intensity, either the states are mixed in roughly equal proportions or the absorption terminating at X^n itself carries some oscillator strength. In either case, X^n emission should appear with intensity comparable to $6^1 10^2$ emission. If $n\nu_x' \sim 1688$ cm^{-1} (the mean frequency of bands a and b is 0,0 + 1688 cm^{-1}) then $n\nu_x'' + \nu_6''$ would be in the vicinity of 2300–2400 cm^{-1}. No prominent $\upsilon_6' = 0$ progression origin is seen at these or any other displacements. Similar arguments apply for a level $X^n Y^n$.

The proposal that the interacting level in the upper state is $6^1 X^n Y^n$ and that its dominant fluorescence $6^1_{0,2} X^n_n Y^n_n$ coincides with $6^1 10^2$ fluorescence is also difficult to reconcile. In the first place, the symmetry restrictions imposed on the combination $X^n Y^n$, if resonance is to occur, require that the combination contains a_{1g}, a_{2g}, or e_{2g}. Second, the observed Franck–Condon envelope for $6^1_{0,2} 10^2_2$ in Figure 12 is consistent with $\upsilon_1' = 0$ and hence any additional intensity due to a second coincident progression must be present in such a way that the intensity profile is not disturbed. This demands that the $6^1_0 X^n_n Y^n_n$ progression origin coincides with $6^1_0 10^2_2$ from which $n\nu_x'' + n\nu_y'' = 2\nu_{10}'' = 1692$ cm^{-1}. The only combination which would satisfy these requirements is $X_n Y_n = 4_1 5_1$. However, ν_4' and ν_5' are known (see previous discussion above) and the calculated position for $6^1 4^1 5^1$ (0,0 + 1640 cm^{-1}) is not sufficiently close to either of the O^0_0 bands (0,0 + 1679 cm^{-1} and 0,0 + 1697 cm^{-1}) to be considered a candidate.

The precise assignment of O^0_0 bands thus remains uncertain although $6^1_0 10^2_0$ is confirmed as being at least partly responsible for their intensity.

Emission from T_{00} + 264 cm^{-1}. An absorption assignment cannot always be established by SVL fluorescence methods and the absorption band at 38,350.2 cm^{-1} is an illustrative case. Atkinson[9] has shown this absorption to be a progression origin but an assignment has not as yet been found.

In Figure 13, the absorption "x" corresponds to the band in question, and it is seen to lie in a region of congestion. Although narrow band excitation has been employed to bias this absorption, the underlying structure arising from the rotational tails of the transitions a and b must also be pumped. The fluorescence spectrum, nonetheless, is relatively simple, and its analysis quickly reveals that the 38,350.2 cm^{-1} absorption transition must be a sequence band of type $6^1_0 X^n_n$. As demonstrated in part I, fluorescence after excitation of a sequence transition of this type is indistinguishable from 6^1 fluorescence. The sequence interval, $n(\nu_x' - \nu_x'')$ is thus ~260 cm^{-1} but no combination of known upper and lower state fundamentals gives rise to this interval. The band is probably too intense to be of type $6^2_1 X^n_n$ and by comparison with the intensities of other known sequence transitions, we suggest that ϵ_{vib} ($^1A_{1g}$) ~ 1000 cm^{-1}. There are several appropriate candidates among the "inactive" fundamentals of benzene but a unique choice cannot be made.

Summary

SVL fluorescence has been shown to be a useful probe in assisting with absorption assignments. New upper state fundamentals have been located and several ambiguities in assignments have been resolved. Table II lists all the absorption assignments established or confirmed by SVL fluorescence.

New Vibrational Frequencies in the $^1B_{2u}$ state. Four excited state frequencies, previously not known, now seem settled. SVL fluorescence confirms or rejects earlier proposals concerning the assignment of absorption bands. This increases the number of secure $^1B_{2u}$ fundamentals from seven to eleven (see Table I, part I).

(i) **$\nu_4' \approx$ 365 cm^{-1}.** SVL fluorescence clearly identifies the proposed[8] second-order Herzberg–Teller transition $4^1_0 10^1_0$. Accompanying evidence concerning the intensity of the analogous transition, $4^0_1 10^0_1$ in zero-point fluorescence,[3] suggests that the Y^0_0 maximum is itself $4^1_0 10^1_0$.

(ii) **ν_5' = 749 cm^{-1}.** SVL fluorescence positively identifies activity in ν_5 as the absorption $6^1_0 5^2_0$ and thereby locates ν_5'. By deduction, a previously unassigned absorption band is identified as $5^1_0 10^1_0$.

(iii) **ν_9' = 1148 cm^{-1}.** SVL fluorescence after pumping the 9^1_0 transition gives a secure assignment for ν_9'. An alternate suggestion that the 9^1_0 absorption may occur as the Y^0_0 band is rejected.

(iv) **ν_{17}' = 712 cm^{-1}.** Atkinson[9] has assigned numerous absorption bands with activity in ν_{17} (transitions 17^2_0, $6^1_0 17^2_0$, $16^1_0 17^1_0$, $11^1_0 17^1_0$, plus various hot-band assignments derived from the last two). SVL fluorescence confirms each of the first three, plus the presence of the absorption $6^1_0 16^1_0 17^1_0$. The absorption 17^2_0 occurs mingled with the A^0_1 band where it has escaped detection in the early absorption studies because of the overwhelming intensity of $6^1_0 1^1_0$ absorption. The absorptions $6^1_0 16^1_0 17^1_0$ and $16^1_0 17^1_0$ give the excited state frequency ν_{17}' = 712 cm^{-1}. The overtone $2\nu_{17}'$ is near 1435 cm^{-1}.[9] These assignments revise the early $6^1_0 17^2_0$ assignment and ν_{17}' frequency given by Garforth and Ingold,[6] but confirm their suggestion of $16^1_0 17^1_0$ absorption in the Y^0_0 band.

Confirmation of Absorption Assignments. SVL fluorescence spectra discussed in Part I are consistent with the long-established assignments of each of the absorption maxima $6^1_0(A^0_0)$, $6^1_0 1^1_0(A^0_1)$, $6^1_0 1^2_0(A^0_2)$, $6^1_0 16^1_1(A^1_0)$, $6^0_1(B^0_0)$, $6^0_1 16^1_1(B^1_0)$, and $6^2_1(C^0_0)$. These bands are found among the more prominent structure in the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption spectrum. Table II identifies 28 additional transitions in the

Table II. Absorption Assignments Confirmed by SVL Fluorescence Spectra

Assignment	Absorption region[a]	Band maximum,[b] cm^{-1} (vac)
6^1_2	D^0_0	37392.5[c]
		37392.7
$6^0_1 11^2_0$	C^0_0	38517.2[d]
16^4_0	Y^0_0	
$16^1_0 17^1_0$	Y^0_0	
$4^1_0 10^1_0$	Y^0_0	39038.5
$6^1_0 16^3_3 1^1_0$	Y^0_0	
$6^1_0 16^2_0$	G^0_0	39082.1
$10^2_0 16^1_1$	G^0_0	
$6^1_0 10^1_1 16^1_1 1^1_0$	G^0_0	
$6^2_1 16^2_2 1^1_0$	G^0_0	
9^1_0		39235.8
10^2_0		39255.0
$6^1_0 11^2_0$	K^0_0	39368.0
6^3_0	K^0_0	
$6^1_0 10^2_0 16^1_1$	K^0_0	
17^2_0	A^0_1	[e]
$6^1_0 16^1_0 17^1_0$	E^0_0	39560.6
$6^1_0 4^1_0 10^1_0$	E^0_0	
$6^1_0 16^4_0$	E^0_0	
$6^1_0 10^2_0$	O^0_0	39783.1[f]
		39765.0
$6^1_0 17^2_0$	B'^0_0	40050.2
$6^2_0 1^1_0$	B'^0_0	
$6^1_0 5^2_0$		40108.9
$6^1_0 11^2_0 1^1_0$	K^0_1	
$6^3_0 1^1_0$		[g]
$6^0_1 2^1_0$		[h]
$6^1_0 10^2_0 1^1_0$	O^0_1	
7^1_0	Q^0_0	41165.3

[a] Refers to the absorption region probed with tuned excitation. Notation after Radle and Beck.[7] [b] Maxima are listed only for those cases where SVL fluorescence spectra can confirm an absorption assignment as applying to a specific absorption maximum. In the remaining cases, SVL spectra show only that the absorption transitions occur in the designated region. [c] Band positions from Callomon, Dunn, and Mills.[8] [d] SVL fluorescence evidence and absorption assignments also discussed in ref 19 and 21. [e] The absorption maximum probably lies near 39,524 cm^{-1}.[9,18] [f] The cause of the splitting has not been established. See text concerning O^0_0 fluorescence. [g] Calculated near 40,578 cm^{-1}. [h] In the region 40,617–46,040 cm^{-1}.

weaker absorption structure which have been confirmed by this SVL fluorescence study. Three other absorption transitions ($6^1_2 1^1_0$, $6^0_1 11^2_0 1^1_0$, and $6^1_0 16^2_1 17^1_0$) have been confirmed by fluorescence after excitation in the C^0_1 absorption region.[19]

"Active" Vibrations. The absorption spectrum and SVL fluorescence spectra show consistently that a set of 12 vibrations is responsible for most of the structure in $^1B_{2u}$–$^1A_{1g}$ radiative transitions. Transitions with quantum changes in other vibrations have not yet been established. The "active" vibrations encompass six of the ten vibrational symmetry species, and every vibration in each of those six species is "active". Vibrations whose $^1B_{2u}$ fundamentals are listed in Table I, part I, comprise, with ν_8, this "active" set. Although transitions with ν_8 excited in the ground state are well known both in absorption and fluorescence, an assignment from which ν_8' may be derived has not yet been secured.[20]

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