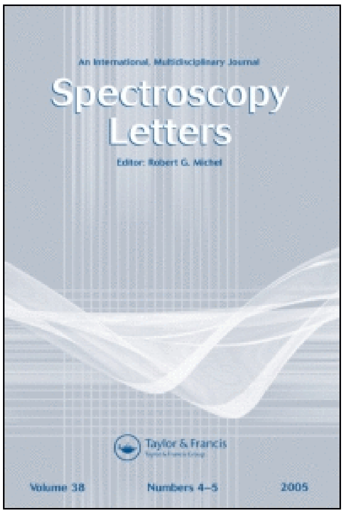

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Emission Spectra Excited in Benzene

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Emission Spectra Excited In Benzene *

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Recently, an emission from molecular benzene has been observed in our electron beam excitation source when benzene was used as a parent molecule for the C_2 molecule [1], the primary subject of our study. Due to the discussion in this journal [2,3] concerning emission excited in a benzene system as observed by Robinson and Rosamund [4], it was felt that our results should be communicated to dispel any ambiguity that may remain for this emission system.

Experimental:

Our apparatus consisted of an rf-modulated electron source, a Seya-Namioka monochromator with a band pass of 5Å, an EMI phototube, and a phase-shift measuring system that has been previously described in detail by Lawrence [5]. Measurement of the phase shift between the input excitation and the resulting emissions yields the lifetime of the upper state of the emitting system. Benzene at pressures up to 120μ was admitted into our source where electrons of up to 400 Volts were used to excite the spectra. Modulation frequencies of 0.96 and 0.54 MHz were used.

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Results:

The molecular benzene emission spectrum excited in the electron source is given in Fig. 1. The results of our lifetime measurements are given in Table I. Donovan and Duncan[6] have previously observed an emission spectrum in benzene excited by an electrodeless discharge under conditions chosen to yield only molecular excitation. The lifetime for emission in the 2620Å to 2720Å region was found to have a lifetime related by the following equation: $\tau^{-1} = 1.69 + 0.0207\ p$, where p is the pressure in microns and τ is the radiative lifetime in nanoseconds. The low spectral resolution of 100Å makes it impossible for the vibrational structure to be observed in their experiment. The band system observed by Robinson and Rosamund[4] overlies this region, but the equivalence of the emissions is not thereby established.

We can now show that both observations originate in the well known $^1B_{2u} \longrightarrow {}^1A_{1g}$ transition in benzene, and that they are not due to an ionic species as suggested by Robinson and Rosamund[4].

Due to the flow system we use, the pressure in the excitation region is at least 20 times smaller than our measured pressure in the sample block, therefore we cannot directly apply a comparison with Donovan and Duncan's value for τ[6], except by an extrapolation to zero pressure. If we do this, we find the values to be in substantial agreement, 590 nanoseconds as measured by Donovan and Duncan[6], and 610 nanoseconds as measured in our experiment, indicating that both arise from the same emitting species.
The trend to shorter lifetimes that we observe at longer wavelengths may represent a variation of lifetime with vibrational quantum number, or could also be due to an overlapping emission from another species blending in at longer wavelengths.

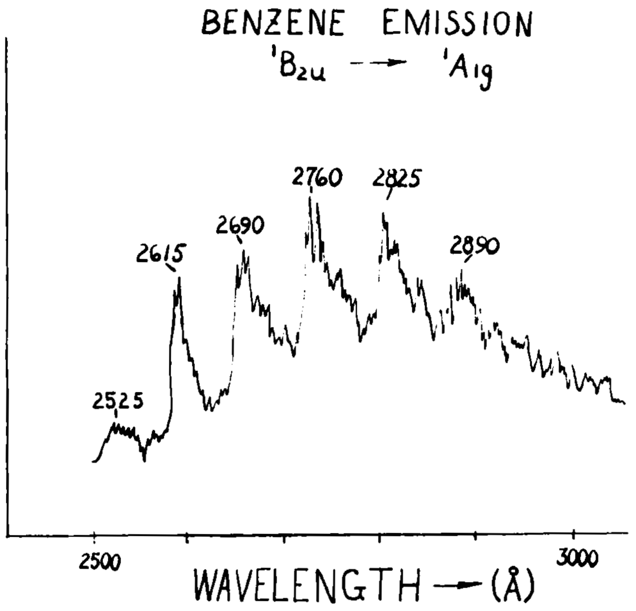

FIGURE 1

Emission Spectrum of Molecular Benzene
in the 2600 Å Region

TABLE I

Molecular Benzene Emission

$^1B_{2u}$ $^1A_{1g}$

Band heads (Å)	τ (extrapolated)	τ (ref. 6)
2525	-	-
2615	-	-
2690	610 nsec.	590 nsec.
2760	530 nsec.	-
2825	400 nsec.	-
2890	-	-

Values are preliminary and approximately ±20%. Details will be given in a separate report.

The vibrational spacing of the band heads in our spectrum given in Table I is essentially the same as that observed by Robinson and Rosamund [4], and has spacing corresponding to a vibrational progression in the a_{1g} ν_2'' (993 cm^{-1}) ring stretching motion of benzene [7]. The apparent shift in wavelength in going from absorption to emission is simply due to the change in position of the minima of the vibrational potential functions in the $^1A_{1g}$ and $^1B_{2u}$ states of benzene. The intensity distribution in emission depends completely upon this relative position due to the Franck-Condon principle, since at pressures of more than a few microns vibrational relaxation is nearly complete by the time most molecules reradiate.

The conclusion that must be reached then is that molecular benzene is responsible for the observed emission in all the instances discussed, even though the means and severity of excitation are significantly different.

REFERENCES

1. W. H. Smith, to be published
2. K. K. Innes, Spectrsc. Letters, 1 (2), 103 (1968)
3. J. W. Robinson, Spectrsc. Letters, 1 (2), 105 (1968)
4. J. W. Robinson and J. D. Rosamund, Spectrsc. Letters, 1 (1), 1 (1968)
5. G. M. Lawrence, J. Quant, Spectrsc. Radiant Transfer, 5, 359 (1965)
6. J. W. Donovan and A. B. F. Duncan, J. Chem. Phys., 35, 1389 (1961)
7. G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Pg. 555, D. Van Nostrand, Princeton, N. J. (1966)