

Rotational Structure of the Near Ultraviolet Bands of Benzene

ANTHONY TURKEVICH* AND MARK FRED

Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

The $\lambda 2300$ – 2800 absorption system of benzene has been photographed in the third order of a 30-foot, 30,000 lines/inch grating. The source of the continuum was a modification of the oxide filament H_2 arc described by Allen.¹ In order to obtain a satisfactory life at an arc current of 20 amperes, the cathode was made of a massive nickel cylinder filled with nickel gauze coated with oxide.² The cathode was brought to operating temperature by a high voltage glow discharge to an auxiliary electrode, after which 220 volts d.c. were applied between cathode and the conventional anode assembly. The arc current kept the cathode hot and the high voltage could then be removed.

Even with the new source the intensity was insufficient to utilize the full resolving power of the grating. Under the best conditions of absorption the resolving power was limited by the slit width to about 200,000. Coarse structure of low contrast was obtained for the B_0^0 , A_0^0 , and A_1^0 bands,³ identical in each but with the contrast decreasing in the above order so that further bands could not be resolved. All bands show a sharp head on the short wave-length side with a fainter head about 6 cm^{-1} to the red and also in the case of B_0^0 about 6 cm^{-1} to the violet (cf. Fig. 1). Toward longer wave-lengths, starting about 12 cm^{-1} from the head, a series of about 50 absorption regions is clearly seen, with spacing increasing regularly from about 0.75 to 1.5 cm^{-1} . Although the structure is thus fairly coarse, there is no trace of it in the first order of the grating.

From the expression for the rotational energy of benzene,

$$E_r = \frac{\hbar^2}{2A} [2J(J+1) - K^2],$$

it is seen that the spacing of the J levels is twice

* Present address: Havemeyer Chemical Laboratory, Columbia University, New York.

¹ A. J. Allen, *J. Opt. Soc. Am.* **31**, 268 (1941).

² We are indebted to Mr. W. G. Taylor, of Taylor Tubes, Inc., for this suggestion.

³ H. Spöner, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Phys.* **7**, 207 (1939).

that of the K levels and they expand in opposite directions. Since the bands degrade to the red, the regular absorption regions might be J structure corresponding to an increase in the moment of inertia in the upper state, or K structure with a decrease twice as great. If one accepts the former interpretation as more reasonable, the variation in spacing gives the change in the reciprocal of the unique moment of inertia A to be $1.82 \times 10^{26}\text{ g}^{-1}\text{ cm}^{-2}$. This implies a 5 percent increase in moment of inertia as a result of the electronic excitation if the electron diffraction data for the ground state are used.⁴

Theoretically the bands should be of a perpendicular type.³ On this basis the regular absorption regions are the heads of the rP branches ($\Delta J = -1$, $\Delta K = +1$) with J varying from around 27 to 73. However, parallel type bands would give similar absorption with the qP branch ($\Delta J = -1$, $\Delta K = 0$) being responsible for the coarse structure. The relation between the variation in spacing and the change in moments is the same on either interpretation. Also in either case the strong head would be formed by the R branch ($\Delta J = +1$), while the faint head to the red side of the strong one may be the maximum in absorption of the Q branch. Since the K structure is unresolved, the probability that the vibration making the electronic transition allowed may involve angular momentum does not affect the interpretation.

Because of very small discrepancies in the vibrational analysis made on the basis of measurements of the band heads,⁵ it would be useful to know the relation of the band origin to the observed head. This has been calculated from the electron diffraction data for the ground state.⁴ The distinguishable parts of the sub-bands (the r heads) come out to lie about 1.6 cm^{-1} to the red of their respective origins. Thus the distance from the main head to the origin of the entire band comes out to be not 3.4 cm^{-1}

⁴ L. Pauling, *Nature of the Covalent Bond* (Cornell University Press, 1939), pp. 158–162.

⁵ H. Spöner, private communication.

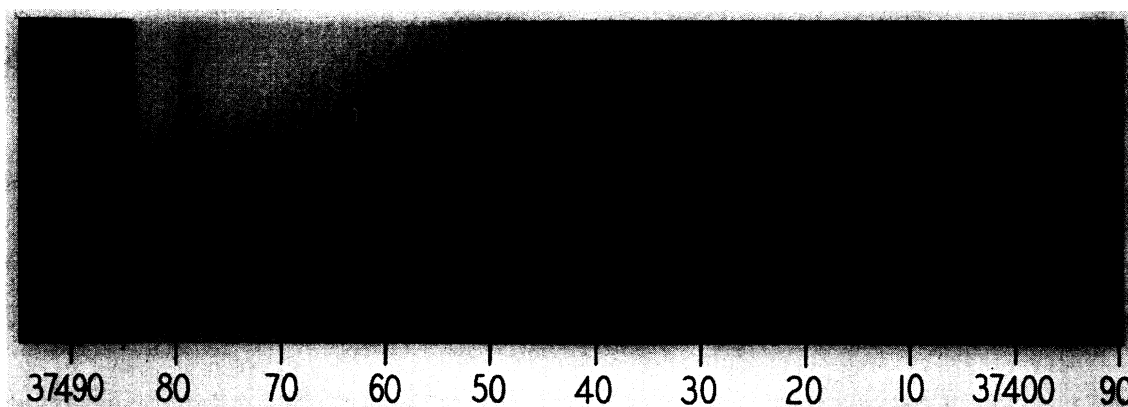


FIG. 1. B_0^0 in the third order of the grating. The emission line at $37,440.3 \text{ cm}^{-1}$ is Fe 4005.25A in the second order.

(given directly by the J structure) but 1.8 cm^{-1} to the red. Under absorption conditions other than those under which the r heads have sufficient contrast to appear above the background, the relation between the observed head and the true origin may be very much different. In agree-

ment with this, the position of the heads has been observed to depend noticeably on the pressure.⁵

We gratefully acknowledge the help of discussions with Dr. H. Sponer, Dr. E. Teller, and Dr. N. Metropolis.

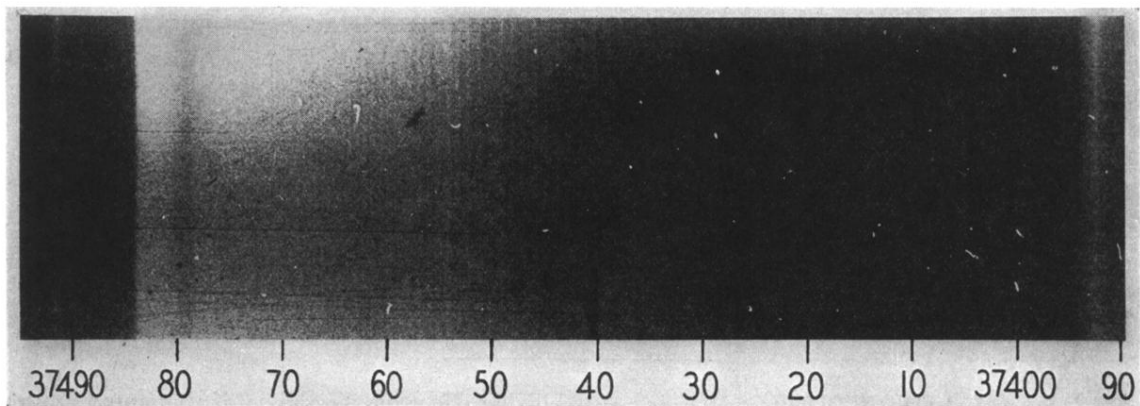


FIG. 1. B_0^0 in the third order of the grating. The emission line at $37,440.3 \text{ cm}^{-1}$ is Fe 4005.25A in the second order.