

Absorption Spectrum of Crystals at Low Temperatures. I

The Effect of Temperature on Spectrum of Benzene and its Monoderivatives*

Eizô KANDA and Ikuji TSUJIKAWA

The Research Institute for Iron, Steel and Other Metals.

(Received Dec. 10, 1949)

Synopsis

We observed the temperature effect of absorption bands in benzene and its monoderivatives, namely monochlorbenzene, monobrombenzene and toluene. There were a displacement of the bands toward the shorter wave-length and a narrowing of the bands, when the temperature was decreased.

About benzene band we studied theoretically the effect of temperature and obtained considerably good results which agreed well with experiments, the band shift is proportional to thermal energy and the half-intensity breadth proportional to a root of thermal energy.

I. Introduction

Previous investigation of the ultraviolet absorption spectrum of various types of solids has indicated that there were a displacement of the bands toward the shorter wave-lengths and a sharpening of the bands when the temperature of the substance was lowered.^(1,2) This phenomenon also has been observed as to spectrum of benzene and its derivatives^(3,4,5,6,7). There has been noticed qualitatively shifts and narrowings of the bands. The present work was undertaken to determine the nature of the shift and the narrowing of the absorption bands in benzene, monochlorbenzene monobrombenzene and toluene within the temperature range between 20°C and -240°C. We noticed that the temperature effect of absorption bands in benzene spectrum can be explained considering the thermal vibration in crystals.

II. Method and Apparatus

The absorption spectrum were photographed with a Hilger E_2 quartz spectrograph. The ultraviolet source was a hydrogen discharge tube, the apparatus being similar to one by Z. Bay and W. Steiner. The vessel containing the specimens under investigation is

* The 546th report of the Research Institute for Iron, Steel and Other Metals.

- (1) A. L. Riemann, *Ann. d. Physik.* **80** (1926), 43.
- (2) O. R. Wulf and E. H. Melvin, *Phys. Rev.* **38** (1931), 330.
- (3) A. Kronenberger and P. Pringsheim, *Zeits. f. Physik.* **40** (1927), 75.
- (4) A. Kronenberger, *Ibid.* **63** (1930), 494.
- (5) I. Obreimow and W. J. de Haas, *Comm. Phys. Lab. (Leiden)* No. 204 (1929).
- (6) A. H. Croup, *Phys. Rev.* **40** (1932), 435.
- (7) W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* **158A** (1937), 634.

shown in Fig. 1. It was a modified Dewar flask, the copper block was soldered to the lower end of the inner cylinder. This connection was a platinum-glass joint and it was possible to evacuate the space between the two cylinders to about 10^{-5} mm Hg pressure at liquid hydrogen temperature. The neck of quartz windows was long enough to keep out of frost.

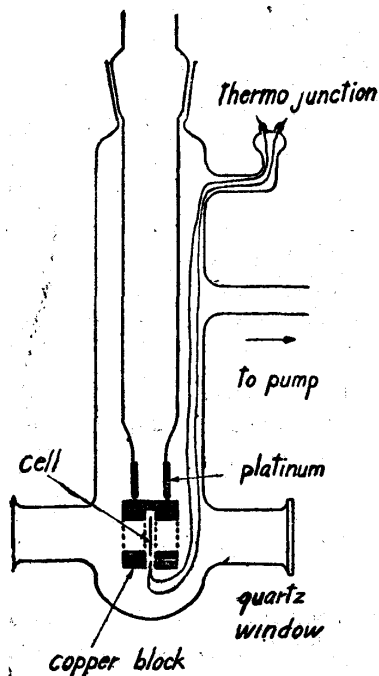


Fig. 1. Cross-sectional view of vessel.

The copper block contained the specimen cell. Due to the high absorbtivity of the specimens, it was necessary to use them in very thin films between quartz disks. The cell, therefore, consisted of two quartz disks pressed together until interference rings were seen. It was then placed in the copper block. To produce the film, a drop of the liquid was placed between the two quartz disks and pressed tightly. It was estimated that the films produced in this way were about 10μ thick.

After the inner cylinder was inserted, the vessel was cooled by pouring in liquid air until the substances solidified. The vessel was then evacuated and the copper block cooled by thermal conduction from liquid air. Temperatures were read by means of a thermojunction. It was possible to keep the temperature constant within 5° range through the exposure time by pouring liquid air drop by drop in appropriate time intervals.

III. Experimental Results

Figs. 2, 3, 4 and 5 show the microphotometer curves obtained from the plates, the absorption spectrum of benzene, monochlorobenzene, monobrombenzene and toluene respectively, where small circles are experimental values. In each case, the absorption bands are broad and diffuse and may be divided into major and minor bands. These bands are labeled by capital letters respectively. The bands shift toward the shorter wave-lengths and become sharper with decreasing temperature. The only one anomaly happens at the longest wave-length band of benzene I_0 , whose intensity decreases by lowering temperature, but due to band broadening by arising temperature, at 150°K this band seems to be most remarkable.

The spectrograms and the microphotometer curves for the monoderivatives show band spectrum similar to those of benzene. The corresponding absorption bands of these compounds are displaced approximately 40\AA toward the longer wave-lengths. The separation between the major bands are greater than those for benzene.

The intensity maxima position and the half-intensity breadth of the bands in benzene

spectra are plotted against temperature in Figs. 6 and 7 respectively. We shall discuss the effect of temperature on the benzene bands (*A* series) in the section V.

IV. Explanation of the Band

(a) Benzene. Sklar⁽⁸⁾ deduced from symmetry considerations that the weak electronic band system between 2300Å and 2800Å is a forbidden one (${}^1A_{1g} \rightarrow {}^1B_{2u}$). The weak intensity of the band system agrees with assignment to a forbidden transition. Spomer, Nordheim, Sklar and Teller⁽⁹⁾ interpreted the longest wave-length band I_0 in Fig. 2 as the 0, 0 band whose appearance is made possible in violation of the selection rules by the

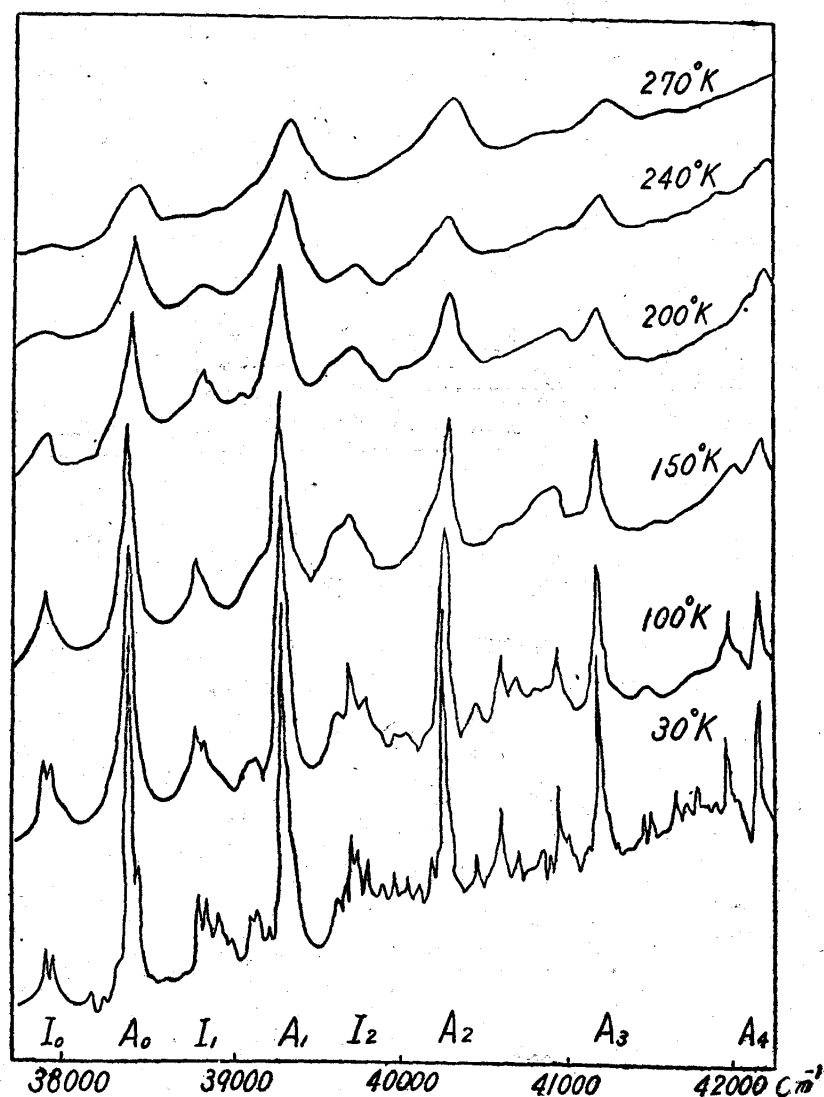


Fig. 2. Microphotometer curves of benzene band.

(8) A. L. Sklar, *J. Chem. Phys.* 5 (1937), 669.

(9) H. Spomer, G. Nordheim, A. L. Sklar and E. Teller, *Ibid.* 7 (1937), 207.

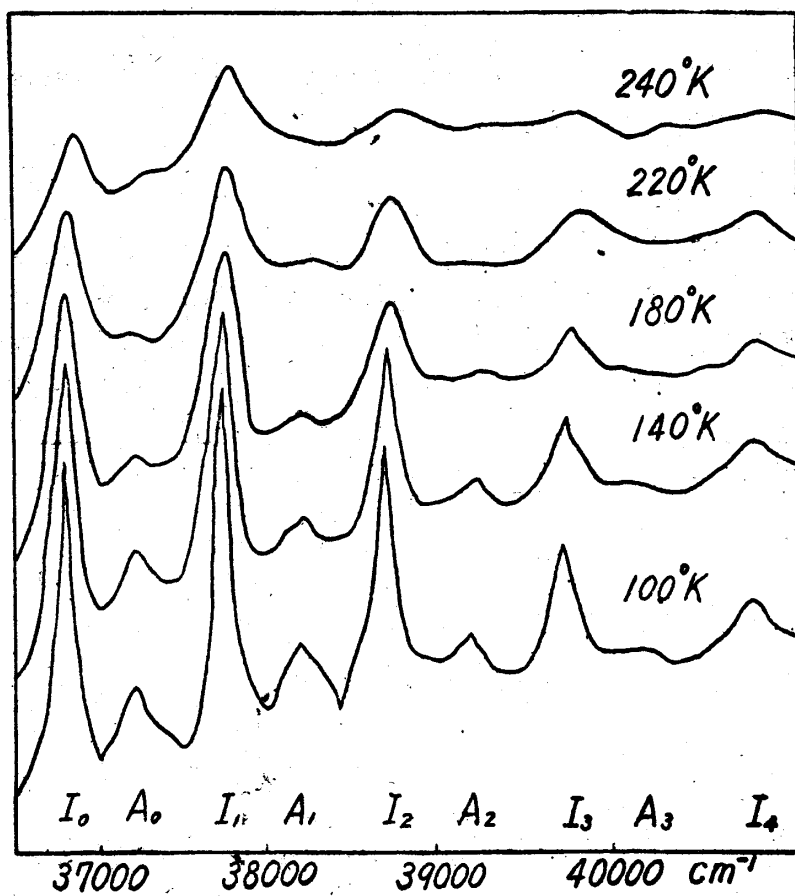
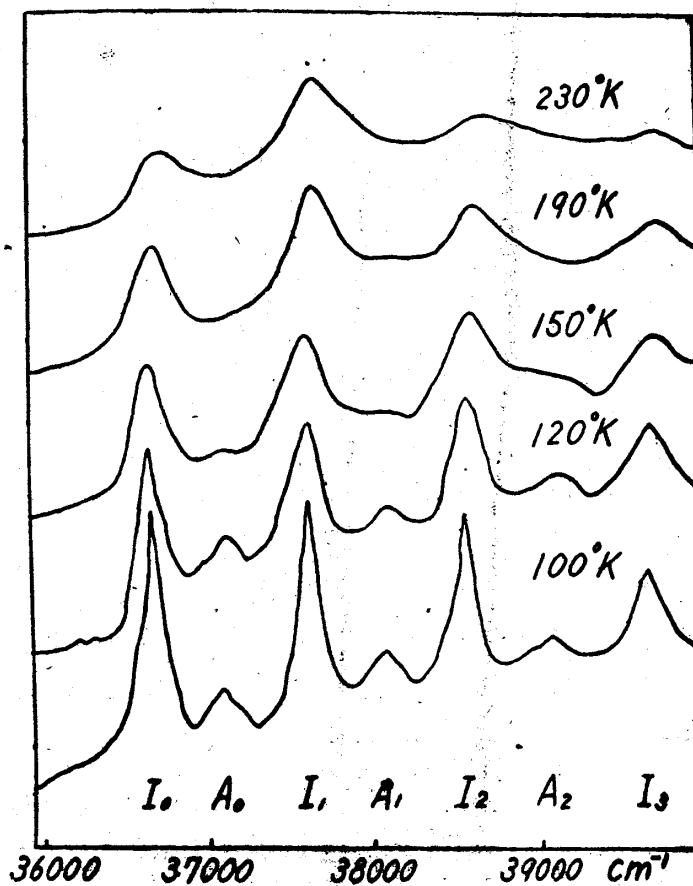


Fig. 3. Microphotometer curves of monochlorobenzene band.

Fig. 4. Microphotometer curves of monobromobenzene band.



action of crystal forces on the benzene molecule. The 0, 0 band is accompanied by a progression of bands spaced from it in multiples of the totally symmetrical vibration 923cm^{-1} (I series). It can be derived⁽¹⁰⁾ that in the case of a forbidden transition, there must occur a change of a nontotally symmetrical vibration of symmetry type E_g^+ (520cm^{-1} in the upper state) by at least one quantum upon which changes of the totally symmetrical vibration are superposed. The perturbation of the electronic level caused by this nontotally symmetrical vibration makes the transition, forbidden for itself, appear with weak intensity (A series).

(b) Monochlorobenzene⁽¹¹⁾, monobromobenzene and toluene. The electronic band system of monoderivatives were considered as an allowed one (${}^1A_1 \rightarrow {}^1B_2$) by Skar⁽¹²⁾. The spectrum of monoderivatives are about two times

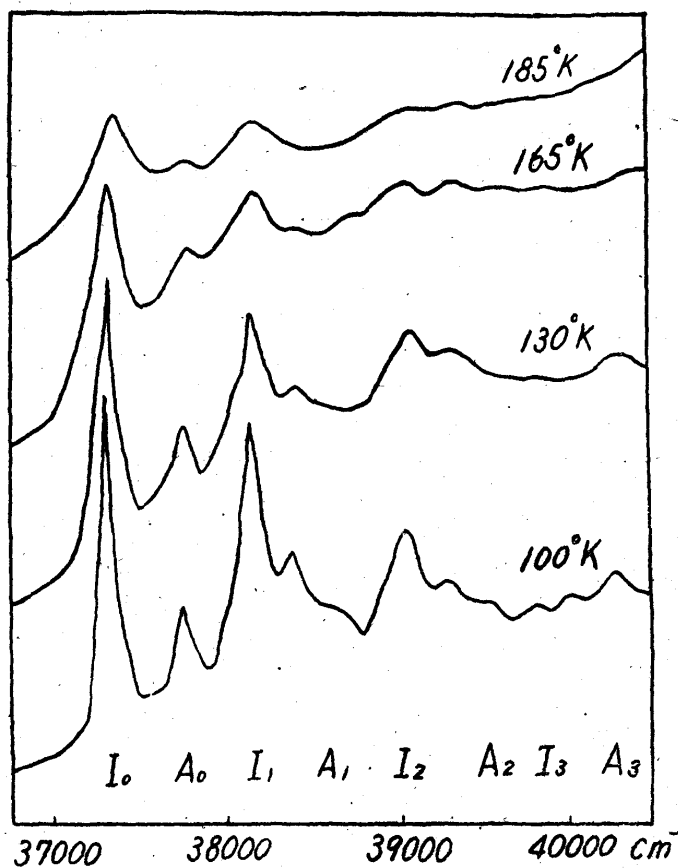


Fig. 5. Microphotometer curves of toluene band.

stronger than the corresponding ones of benzene and naphthalene which are forbidden. In agreement with the assignment to allowed transitions, the 0, 0 band I_0 appears in each monoderivative spectra. It is therefore not impossible that the mechanism which brought the benzene spectra into appearance at high intensity, namely the excitation of an E_g^+ vibration remains important in them. In this connection the longest wave-length band of the second group of the spectrum A_0 is tentatively associated with the corresponding vibration in the monoderivatives.

V. The Effect of Temperature on the Benzene Bands

Peierls⁽¹³⁾ studied the nature of band shift and breadth change of the absorption band of solid due to lattice vibration, where he pointed out that the band shift is pro-

(10) G. Herzberg and E. Teller, *Zeits. f. Physik. Chemie.* B21 (1933), 410.

(11) H. Spöner and S. H. Wollman, *Phys. Rev.* 57 (1940), 1078.

(12) A. L. Sklar, *J. Chem. Phys.* 7 (1939), 984.

(13) R. Peierls, *Ann. d. Physik.* 13 (1932), 905.

portional to thermal energy (and the half-intensity breadth proportional to a root of thermal energy) in the case of simple cubic lattice. We shall now develop his theory and apply it to the case of benzene, taking some approximation.

According to Peierls's theory, the band shift is

$$\frac{D^0 + J^0}{\omega_0^2 M a^2} E(T) \quad (1)$$

where, D^0 and J^0 mean exchange and Coulomb integrals respectively, which express the interaction energy between nearest atoms; ω_0 , Debye frequency multiplied by 2π ; M , mass of an atom; a , lattice constant; E , thermal energy due to lattice vibration.

And the half-intensity breadth is

$$\frac{\sqrt{D^{02} + J^{02}}}{\omega_0 \lambda \sqrt{M}} \sqrt{E(T)} \quad (2)$$

In approximation, we take van der Waals energy between nearest molecules as $D^0 + J^0$ or $\sqrt{D^{02} + J^{02}}$, because interaction energy is that one in case of molecular crystal, also mass of a benzene molecule as M , lattice constant in the direction of b -axis as a , and total thermal energy containing molecular vibration as well as lattice one as $E(T)$. We introduce the numerical value of the van der Waals energy from the calculation by de Boer⁽¹⁴⁾, a from X-ray data by Cox⁽¹⁵⁾ and ω_0 from specific heat data by Ahlberg, Blanchard and Lundberg⁽¹⁶⁾. Thus we obtain as the constants of formula (1) and (2), 2.0×10^{-2} and 3.1×10^{-7} in c.g.s. unit, respectively.

The solid curves in Fig. 6 are plotted by the formula

$$h\nu = h\nu_0 - cE(T) \quad (3)$$

where, ν mean frequency, ν_0 that extrapolated to 0°K in each band and c is 3.3×10^{-2} being suitable for experimental results, namely, the band shift is order of percent of thermal energy. We use the value of $E(T)$ from the specific data also⁽¹⁶⁾.

The solid curves in Fig. 7 are plotted by the formula

$$\Delta h\nu = \Delta(h\nu)_0 + c' \sqrt{E(T)} \quad (4)$$

where, $\Delta h\nu$ means half-intensity breadth in energy, $\Delta(h\nu)_0$ that extrapolated to 0°K in each band and c' is 6.2×10^{-7} in c.g.s. unit being suitable for the experimental results. Then $\Delta(h\nu)_0$ obtained from experiment, consists of besides the natural breadth of band, the breadths from the slit of the spectrograph and the microphotometer.

In both cases, the solid curves agreed well with experimental values at comparatively low temperatures below 200°K . The constants in our approximation, 2.0×10^{-2} and 3.1×10^{-7} are compared with the ones in experimental curves, 3.3×10^{-2} and 6.2×10^{-7} res-

(14) J. H. de Boer, *Trans. Farad. Soc.* 32 (1936), 10.

(15) E. G. Cox, *Proc. Roy. Soc.* 135A (1932), 491.

(16) J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, *J. Chem. Phys.* 5 (1937), 539.

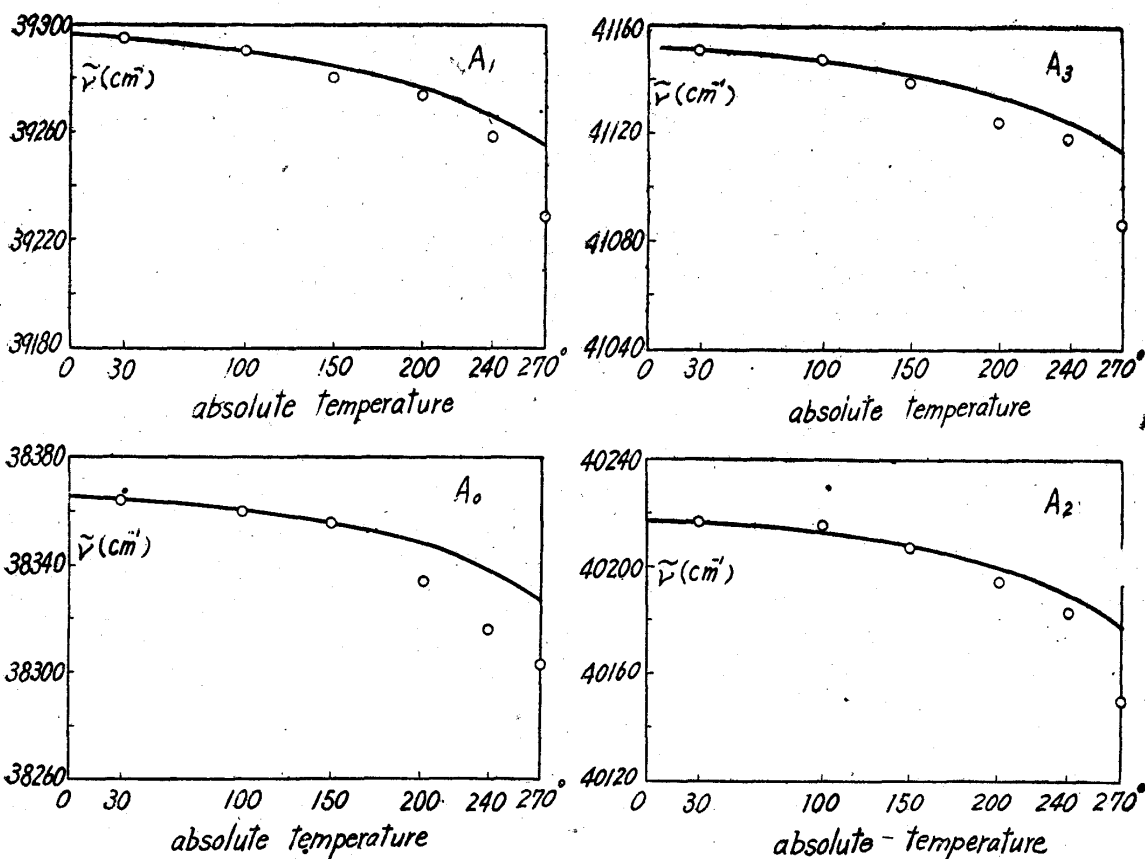


Fig. 6. Frequency—temperature curves of benzene band (*A* series).

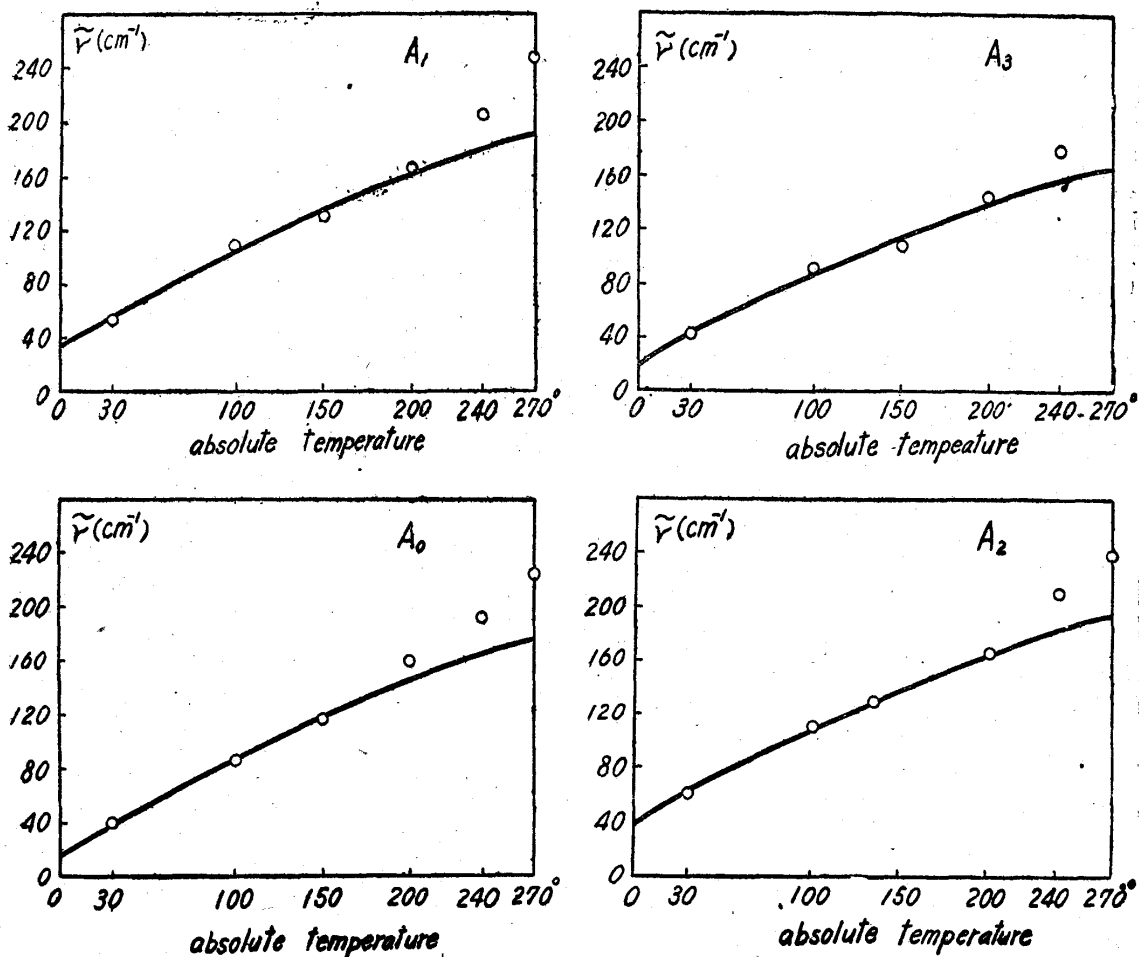


Fig. 7. Halfintensity breadth—temperature curves of benzene bands (*A* series).

pectively, the result is satisfactory for such rough approximation. Disagreement of curves with experimental values above $200^{\circ}K$ is probably ascribed to the overlapping effect of neighbouring bands due to broadening and to neglecting the effect of thermal expansion which must not be ignored in molecular crystals theoretically.

In conclusion we noticed that the effect of temperature on benzene band can be explained by application of Peierls's theory to this problem which is concerned with molecular crystal. In addition to this view the effect of thermal expansion on spectrum should be studied in future.

This research has been aided by the Scientific Research Expenditure of the Department of Education.