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Doppler-free two-photon absorption spectroscopy of the $\tilde{A} \leftarrow X$ transition of C_6D_6 molecule

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[Introduction].

One of the fundamental problems in the spectroscopy and the understanding of the dynamics of ployatomic organic molecules is the onset of channel three in benzene. This deviation might be explained by intramolecular vibrational relaxation (IVR) prior to electronic relaxation in this excess energy range. Partitioning of IVR has been studied by measurement of the quantum yield of fluorescence and the lifetime of the excited state. Because most of these measurements were carried out by exciting many rotational lines simultaneously, we need to high-resolution technique to resolve rotational quantum states of the excited levels in detail. This problem can be achieved using Doppler-free two-photon absorption spectroscopy, and this technique has been applied to study the $A^1B_{2u} \leftarrow X^1A_{1g}$ transition of benzene firstly. In this experiment , we were able to show that the relaxation behavior of benzene in the channel three region is strongly dependent on the rotation of the molecule. For example, Coriolis coupling seems to be responsible for the absence of many rotational lines in benzene. In this work, the DFTPA spectra and the Zeeman effects of the $14^1_0 1^1_0$ vibronic band of banezene-d_6 have been measured.

[Experimental].

The rotational spectra of benzene-d_6 are obtained by employing Doppler–free two-photon spectroscopy. The vapor pressure of benzene-d_6 at room temperature is ~45 mTorr and the sample of purifing via freez melt saw was introduced into the experimental cell. As a light source we employed a single mode ring dye laser (Coherent CR 699-21) operated with Coumarin102 dye and pumped by the violet lines of a Kr^+ laser. The light beams are counterpropagated to identical wavelength within an external cavity. The absolute frequency position of the fringe marks were calibrated by measuring the Doppler-free saturation spectrum of $^{130}Te_2$. For Zeeman experiments, Zeeman effect could be obtained with a maximum field of 1.2T. The magnetic field was applied perpendicular to the propagation vector of the laser beam.

[Results and Discussion].

Rotationally resolved structure of the $14^1_0 1^1_0$ vibronic band in the $A^1B_{2u} \leftarrow X^1A_{1g}$ electronic transition of benzene-d_6 has been investigated with the technique of Doppler-free two-photon (DFTPA) spectroscopy. The width of the spectral line was observed to be approximately 12 MHz. A portion of the observed spectrum is depicted in the Figure. Only Q_Q lines were observed, and the transition energies depend on only differences in the molecular constants between the excited and the ground state. A series of spectral lines were readily assigned from their regular energy spacing.

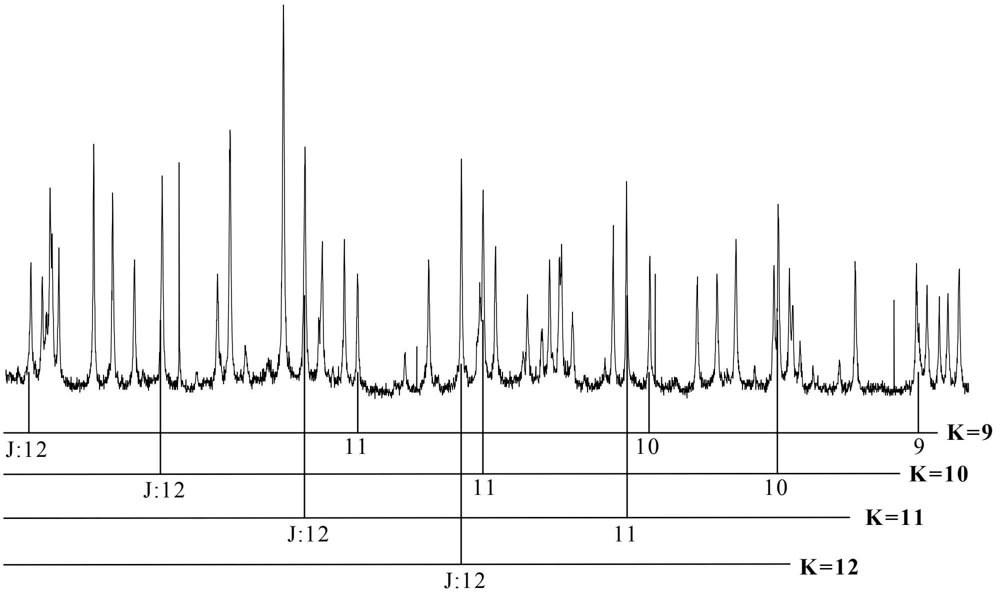

Figure. Doppler-free two-photon absorption spectrum. Assignments of $Q(J)_{Q(K)}$ lines for K=9-12 are shown below the spectrum, while other $Q(J)_{Q(K)}$ lines are indicated above the lines as J_K.