

4P062 Doppler-free two-photon excitation spectroscopy and the Zeeman effect of $14_0^1 1_0^1$ of C_6D_6 molecule

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[Introduction].

Doppler-free two-photon excitation (DFTPE) spectrum of the $14_0^1 1_0^1$ band of the $S_1 \ ^1B_{2u} \leftarrow S_0 \ ^1A_{1g}$ transition in the benzene- d_6 molecule was measured by Sieber *et al.* They reported that the rotational structure of the $14_0^1 1_0^1$ band had not been able to analyze and only the $J = K$ lines were seemed to be in the neighborhood of the expected positions. Dispersed emission spectra from single rovibronic states were also measured after DFTPE, and it was demonstrated that the coupling is very selective and far from the statistical limit. More extensive studies on this complicated spectrum may be able to get more information on the dynamics in the excited state. The Zeeman effects have been demonstrated to be very useful not only to study the perturbation between a singlet state and a triplet state but also to assign a complicated spectrum. We have measured the DFTPE spectrum and the Zeeman effect of the $14_0^1 1_0^1$ band of C_6D_6 with counter-propagating light beams of identical wavelength within an external cavity. This band is confirmed to be strongly perturbed, but regular energy shifts are found and a number of lines are in the regular energy spacing.

[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 purifying via freeze 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].

The DFTPE spectrum and the Zeeman effect ($H = 1.2$ T) of the C_6D_6 were measured from 40723.7 to 40734.0 cm^{-1} . This band is strongly perturbed and difficult to assign at a first glance. Since it was reported that it had not been able to analyze and only the $J = K$ lines were seemed to be in the neighborhood of the expected positions, we could assign every line of appreciable intensity in the range from the band origin 40733.8 cm^{-1} to 40731.4 cm^{-1} and the assignment are indicated in Fig. 1. The lines in this region were found to be perturbed centered at $K = 2 - 3$. The perturbation was identified as originating from interaction between two states. From the deperturbation analysis, the perturbation was shown to be originating from anharmonic coupling between two nearby states. In the region of $40731.4 - 40723.7$ cm^{-1} , the assignments of some lines were difficult. Some lines could not be assigned even those were observed with appreciable intensities, and the examples can be seen in Fig. 2. Zeeman splittings of some lines of large J and K became large and overlapped with other lines. However, the spectral lines are not chaotic, and the perturbations seems to be originating from accidental coincidence between two or three states. The Zeeman splittings of the $^{Q(K)}Q(J)$ lines of a given J were observed to increase proportionally to K^2 and the Zeeman splittings of the $^{Q(K)}Q(J)$ lines to increase proportionally to J . These are coincident with the ones observed in the 14_0^1 band of C_6D_6 . The Zeeman splitting of the $^{Q(40)}Q(40)$ line at $H = 1.2$ T was observed to be 0.0058 cm^{-1} in the present study, while the corresponding Zeeman splitting in the 14_0^1 band of C_6D_6 was 0.0069 . The magnitudes could be explained satisfactory as the Zeeman splittings are originating from the electronic orbital angular momentum arising from mixing of the $S_1 \ ^1B_{2u}$ and $S_2 \ ^1B_{1u}$ states by the $J - L$ coupling (electronic Coriolis interaction). No perturbation originating from an interaction with a triplet state was observed. Intersystem mixing between singlet and triplet states is not likely in lower vibrational states of a isolated benzene, and intramolecular vibration-rotation mixing will be primary process in the intramolecular energy transfer.

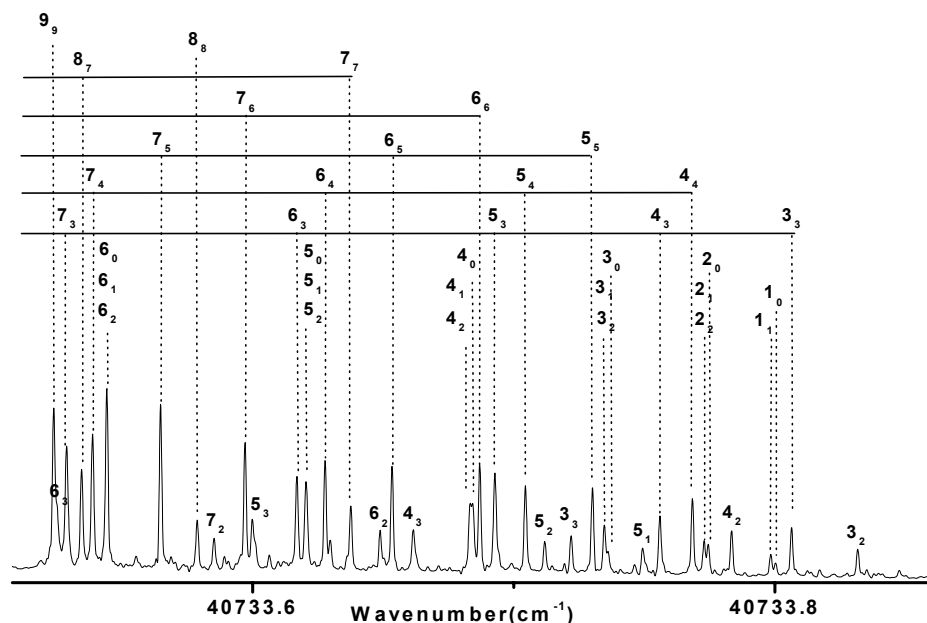


Fig. 1. Doppler-free two-photon excitation spectrum around the band origin of the $S_1 \ ^1B_{2u}(v_{14} = 1, v_1 = 1) \leftarrow S_0 \ ^1A_{1g}(v = 0)$ transition of benzene- d_6 . Assignments of the $Q^{(K)}Q(J)$ lines are indicated as J_K above the spectral lines marking with dotted lines, while those without dotted lines are transitions to perturbing lines.

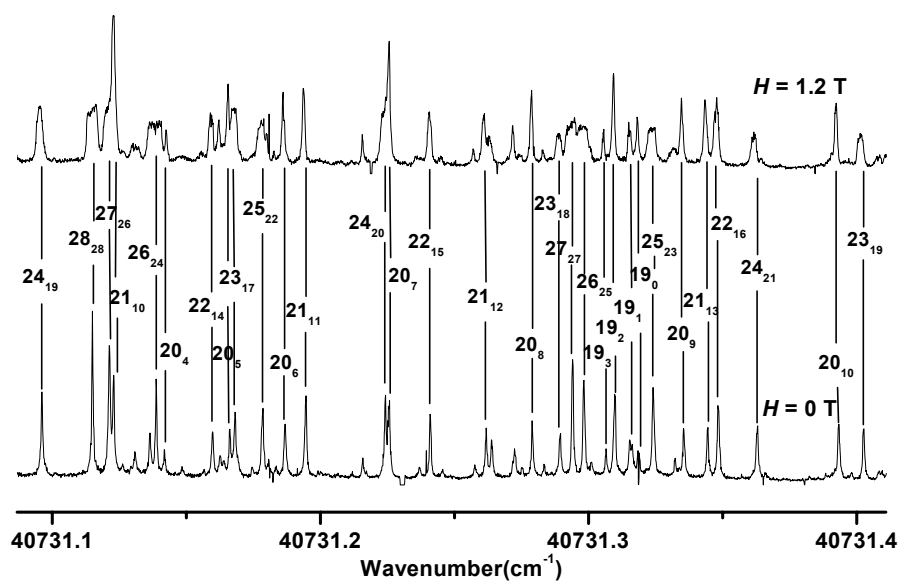


Fig. 2. Doppler-free two-photon excitation spectra of benzene- d_6 in the regions of 40731.09 - 40731.42 cm^{-1} at the magnetic field $H = 1.2 \text{ T}$ and $H = 0 \text{ T}$. Assignments of the $Q^{(K)}Q(J)$ lines are indicated as J_K .