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# Laser Spectroscopy VI

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# Doppler-free Two-Photon Electronic Spectra of Large Molecules with Resolution Near the Natural Linewidth

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The method of two-photon spectroscopy with counterpropagating light beams was predicted by Vasilenko et al. /1/ to yield extremely resolved Doppler-free electronic spectra. This was experimentally realized for Na atoms as soon as dye lasers of sufficient resolution were available /2/. For large polyatomic molecules this experiment was for the first time performed successfully by our group for the prototype molecule benzene ( $C_6H_6$ ) /3/ using a cw dye laser and an  $Ar^+$  ion laser providing the two photons of nearly equal wavelength. The resolution of 80 MHz was sufficient to resolve most of the rotational lines normally hidden beneath the Doppler broadening. Subsequently we were able to use a pulsed laser system of nearly Fourier-transform-limited bandwidth for these experiments providing a large increase in sensitivity /4/. Now we are able to record the two-photon spectra with a single high power cw ring dye laser. The observed linewidth of as low as 10 MHz (instrumentally limited) enables us to resolve all rotational transitions.

In recent experiments we started to investigate the collisionless linewidth of single rotational lines within the electronic spectrum of the polyatomic molecule benzene. The linewidth measured under collision-free conditions is expected to yield precise information about the time constant of intramolecular relaxation processes within the molecule.

In order to improve the signal-to-noise ratio in our experiments at low pressures and to increase the accuracy of the linewidth measurements these Doppler-free two-photon experiments have been performed in an external concentric cavity as shown in Fig. 1. The signal enhancement made possible by an external cavity has been demonstrated previously for the measurement of two-photon Ramsey fringes /5/ and pressure-broadening and -shifts in rubidium /6/. With a piezo-mounted spherical end mirror of 99% reflectivity and a spherical front mirror ( $r=100\text{mm}$ ) of 70% reflectivity we measured a finesse of about 8. To lock the external cavity to the varying laser frequency, the mirror separation is slightly modulated. The resulting amplitude modulation of the transmitted light is fed into a phase-sensitive servo-loop. With the external cavity the signal of the Doppler-free two-photon absorption is larger by about one order of magnitude as compared to the standard set-up. Now we are able to measure single rotational lines in the benzene two-photon spectrum at pressures as low as 0.1 torr.

In order to obtain information about the nature of the intramolecular relaxation process it is important to investigate that process as a function of excess energy within the  $S_1$  state. Particularly for the prototype organic molecule benzene it has been found from lifetime and quantum yield measurements that the rate for intramolecular relaxation increases drastically with the excess energy of the excited vibration /7/. In addition our recent Doppler-free two-photon spectra /8/ indicate that there is also a strong dependence of the radiationless process on the rotational state within a given vibrational state. To investigate the influence of vibrational excess energy, the same rotational transition has been

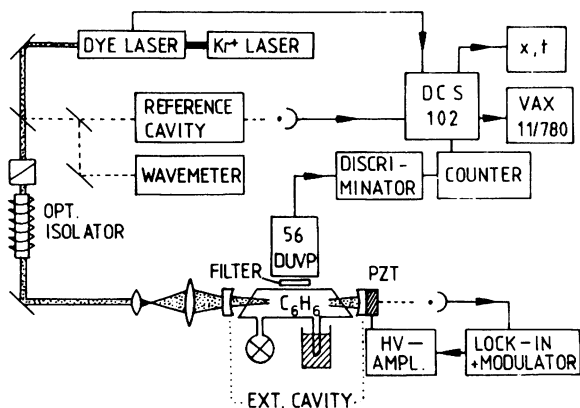


Fig.1 Experimental set-up for recording Doppler-free rotationally resolved two-photon spectra of  $C_6H_6$ . For signal enhancement an external concentric cavity is used

measured for two vibronic bands of the same symmetry, however, of different excess energies. The result is shown in Fig.2. At the bottom part of the Q-branch ( $\Delta J=0$ ,  $\Delta K=0$ ) of the  $14_0^1 1_0^1$  vibronic band of benzene is shown under high resolution as measured with the set-up of Fig.1. Every line in the spectrum corresponds to a single rotational transition which has been assigned by symmetric rotor calculation. For demonstration the K-structure of the  $J=10$  sub-branch is marked in this spectrum. A particular rotational line ( $J=10$ ,  $K=0$ ) of the  $14_0^1 1_0^1$  transition is shown on an extended frequency-scale ( $\times 10$ ) when recorded under the low pressure of 0.1 torr where collisional broadening does not contribute

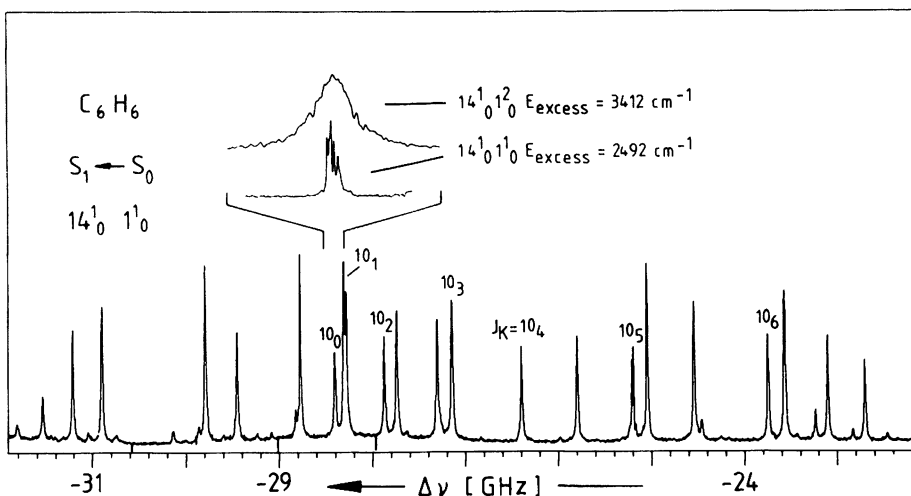


Fig.2 Part of the Doppler-free two-photon spectrum of the  $14_0^1 1_0^1$  vibronic band in  $C_6H_6$ . The lineshape of a particular rotational transition  $J=10$ ,  $K=0$  is shown on an extended scale for two different vibrational excess energies

to the linewidth. The measured linewidth of 10 MHz is mainly given by the spectral resolution of our set-up (the laser linewidth and transit-time broadening), so that the collisionless linewidth is expected to be far below 10 MHz for this excess energy ( $2492 \text{ cm}^{-1}$ ).

For comparison, above this line, the lineshape of the same rotational transition  $J=10, K=0$  is shown as recorded in the  $14_0^1 1_0^2$  vibronic band (excess energy of  $3412 \text{ cm}^{-1}$ , sample-pressure of 1.1 torr). Even after correction for the residual pressure broadening, the collisionless linewidth is found to be broader by at least a factor of three. The derived value of 30 MHz is far greater than the instrumental resolution so that it represents the collision-free linewidth of this rotational transition.

In another series of experiments the linewidth has been measured as a function of the rotational quantum number  $J$  for  $K=0$  lines of the same vibronic band  $14_0^1 1_0^2$  at constant vibrational excess energy. We found a three-fold increase of the linewidth from  $J=2$  (26MHz) to  $J=14$  (74 MHz) pointing to a strong dependence of radiationless processes on the rotation of the polyatomic molecules.

In conclusion, we have previously shown that rotations play an important role in intramolecular relaxation processes of polyatomic molecules. Elimination of the Doppler broadening is essential for these molecules, to resolve single rotational transitions. To be able to study the influence of rotations in a quantitative way, it is essential to increase the experimental resolution to the point where the collisionless linewidth of single rotational transitions can be measured. This has been done for the first time for a polyatomic molecule, benzene ( $\text{C}_6\text{H}_6$ ). Strongly differing linewidths were observed within one vibronic band. This clearly demonstrates the importance of Doppler-free high resolution two-photon spectroscopy for the spectroscopy and exact study of the dynamic behaviour of molecules.

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