# Probing Benzene in a New Way: High-Resolution Time-resolved Rotational Spectroscopy†

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Precise values for the rotational constants of benzene in both the ground and the electronically excited state have been obtained by time-resolved rotational spectroscopy. A relative uncertainty on the order of $10^{-5}$ for these constants has been achieved, while the absolute values are in excellent agreement with data from rotationally resolved optical spectroscopy. Thus benzene serves as a molecular benchmark for high-resolution rotational coherence spectroscopy (RCS) with the perspective that the influence of vibrations on the equilibrium structure could be studied for a medium-sized molecule by this method soon.

## Introduction

Benzene is an archetypical molecule in chemistry, which has been studied for many years in Ed Schlag's group with great scrutiny. The fruits of these investigations have been many significant breakthroughs in the methodology of modern laser spectroscopy, such as multiphoton mass spectrometry,[1] Doppler-free two-photon excitation spectroscopy[2] or zero kinetic energy electron spectroscopy (ZEKE).[3]

In this account the spectrum of a high-resolution rotational coherence spectroscopy (RCS) investigation of benzene is presented and compared with data from high-resolution frequency-resolved experiments. Our measurements represent the first RCS results on this prototypical aromatic molecule. Benzene has been the subject of many spectroscopic investigations by various methods and can be envisaged as a molecular benchmark system for high-resolution techniques. The work of Callomon et al.,[4] more than 30 years ago, still represents a very good resolved one-photon UV spectrum of benzene, resulting in an excited-state rotational constant of 5426(15) MHz. Since that time experimental techniques have improved and new methods have become available. For instance, the first two-photon Doppler-free spectrum for a polyatomic molecule has been measured for benzene by Schlag and co-workers.[2] For a further summary of spectroscopic results on benzene, see the work of Hese and co-workers[5] and references therein. Experimental methods applied involve high-resolution IR spectroscopy for the electronic ground state and rotationally resolved UV spectroscopy for the electronically excited state. Microwave experiments have not been reported for this system, because it has no permanent dipole moment due to its high symmetry ($D_{6h}$). However, benzene-$d_1$ and the benzene-argon cluster have been studied by microwave[6a,b] and rotationally resolved UV spectroscopy.[7]

Riedle et al.[8] obtained a high-resolution one-photon UV excitation spectrum of jet-cooled benzene on the $6_0^1$ and the $6_0^1 1_0^1$ bands at 259 and 253 nm, respectively. They used ground-state data, determined by Pliva and Pine[9] with IR spectroscopy, to fit the excited-state rotational constants to their spectrum. A series of IR investigations that followed pointed to a $B$ rotational constant for the ground state that is ≈0.3 MHz higher than the result of ref 9 (see refs 3 and 10 for a compilation). The difference of more than 20 standard deviations is now attributed to a calibration error or a misassignment in the partially unresolved Q branches.[8] A recent investigation was performed by Hese and co-workers fitting ground-state and electronic excited-state rotational constants simultaneously to their high-resolution UV data.[5] Their work confirms the recent IR studies for the ground state and gives also highly accurate values for the rotational constants of the electronic excited state, with a relative uncertainty of 0.002% on the $2\sigma$ confidence level. Correcting the earlier UV spectroscopic results with the 0.3 MHz offset, or comparing the difference between the ground-state and the excited-state $B$ rotational constant [$\Delta B = (B'' - B') =$ 239.266 MHz[6] and $\Delta B$ = 239.349 MHz],[5] gives a good agreement between both measurements. The measurements of Hese and co-workers allowed also for a fit of higher order terms such as Coriolis coupling constants and corrections due to centrifugal distortion.

Due to the high quality of the available spectroscopic data, benzene is an ideal test system for a benchmark study for high-resolution RCS to test both the precision, i.e., the uncertainty, and the accuracy, i.e., the correctness, of the rotational constants obtainable with our experimental setup. Moreover, the applied technique of time-resolved fluorescence depletion (TRFD) is not preferentially sensitive to the change of the rotational constants upon electronic excitation but instead to their absolute values. Hence, provided a high time resolution, the determination of the rotational constants of both the electronic ground and excited state from one experimental trace are enabled. Benzene is known as an oblate symmetric top with the $C_6$ axis being the top axis and a perpendicular transition dipole moment for the $S_1 \leftarrow S_0$ $6_0^1$ transition at 38 606 cm$^{1}$, whereas the vibrationless $0_0^0$ transition is symmetry-forbidden. The high symmetry of benzene has been confirmed by UV spectroscopic results, giving $(A' - B') \leq 50$ kHz.[5] Therefore $A = B$ can be safely assumed, as has been done in this and the cited preceding investigations. With the further assumption of planarity, the equation $I_C = I_A + I_B$ holds for the moments of inertia and one obtains $C = B/2$. Therefore the determination of one rotational constant is sufficient to describe the structure of the electronic ground state or the excited state.

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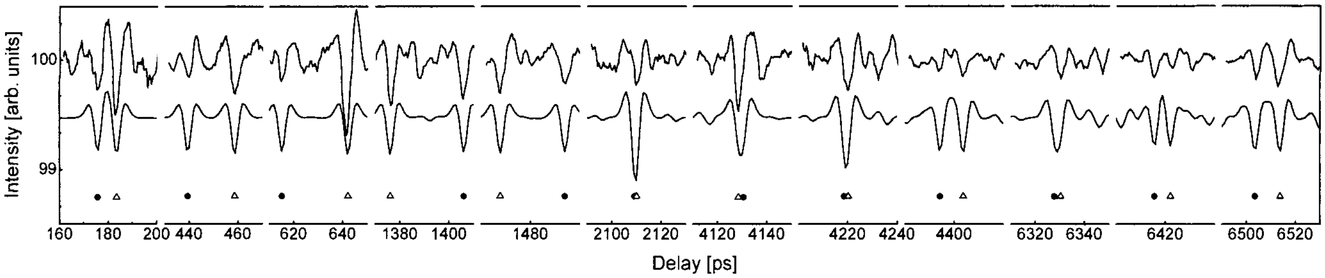

**Figure 1.** High-resolution RCS measurement of benzene. Twelve selected and magnified parts of the TRFD RCS spectrum are given. The upper trace represents the experimental data, and the lower trace, the simulation. *J*-type transients of the ground state and the electronic excited state have been identified and their positions are marked by • and △, respectively. Note that the widths of the RCS transients is only ≈3.5 ps, resulting in a high precision for the derived rotational constants.

## Experimental Section

In this work we applied a time-resolved spectroscopic technique, namely, rotational coherence spectroscopy (RCS), to investigate the rotational quantum beats of benzene in a pump−probe fluorescence experiment in order to determine the corresponding rotational constants. RCS has been described in the literature for several experimental implementations in detail.[11] For this report it is sufficient to recapitulate that it delivers transient spectroscopic signals, which can be related to the recurrence of an initial alignment reflecting the coherent excitation by an ultrashort linearly polarized laser pulse. These recurrences can be followed over several periods in time by a polarization-sensitive probe process and are related directly to the rotational constants (or combinations thereof) of the system under study. In particular, for benzene, similar to a diatomic molecule, *J*-type recurrences with $t_J = n/(4B)$, $n = 1, 2, ...$, are expected in an RCS spectrum. Additionally *K*-type and *C*-type recurrences are expected with $t_K = n/|4C - 2(B + A)|$ and $t_C = n/(4C)$, assuming a perpendicular transition for the pump and the probe pulse.[11] With the symmetry constraints from above ($A = B$, $C = B/2$), $t_C = t_K = n/(2B)$ is obtained. Therefore the even recurrences of the *J*-type transients are superimposed by *K*-type and *C*-type transients of the same polarity. Simulations showed that each transient type shares a third of the total modulation intensity.

In particular, we applied an implementation of RCS, i.e., time-resolved fluorescence depletion spectroscopy (TRFD),[12] where in a pump−probe experiment after photoexcitation the recurrence of the initial alignment is probed by a second laser pulse and recorded by integrated laser-induced fluorescence. Pump and probe pulse are generated in an interferometric setup, so that they have the same wavelength, energy, and polarization.

For this TRFD RCS study a seeded continuous supersonic expansion of benzene ($C_6H_6$) was maintained at a stagnation pressure of 1.5 bar of helium. The sample reservoir was kept in a gas mixing unit at 280 K. Experiments have been performed also with the perdeuterated species ($C_6D_6$) to confirm the assignment of the observed transients. The experimental setup has been described before.[13,14] It consists of a solid-state picosecond UV laser, that delivers ≈2 ps pulses with ≈30 $\mu$J of energy, bandwidth ≈ 10 cm$^{-1}$, running at 500 Hz, and a molecular beam apparatus equipped with a detection scheme for laser-induced fluorescence. The measurements were performed as one-color TRFD experiments on the $S_1 \leftarrow S_0\ 6_0^1$ transition at 38 606 cm$^{-1}$ of benzene and the corresponding transition of the perdeuterated species at 38 786 cm$^{-1}$. A long-pass filter reduced stray light in front of the photomultiplier. The UV pulses were focused with an $f = 200$ mm lens into the expansion at about 2 mm distance from the nozzle. The data were averaged over 500 points per delay line setting, and a step size of 0.5 ps has been used because of the small width of the transients of only 3.5 ps. More than 50 sections around transient positions have been scanned, recording more than 80 *J*- type transients of the ground state and the electronic excited state. Ten or more scans in alternating directions have been performed for each section and smoothing of the raw data with 2.5 ps adjacent averaging was employed. Only the negative-going recurrences of the *J* transients have been considered, because of their higher modulation intensity in comparison with the positive-going recurrences.

## Results and Discussion

Figure 1 shows some selected sections of the experimental data. Note the width of 40 ps for each section and that the average modulation amplitude is only around 0.25% of the total fluorescence signal. Features of the ground state (labeled by •) and the electronically excited state (labeled by Δ) are identified in comparison with data from the literature; namely, B″ > B′ and therefore $t_J'' < t_J'$. Because of the long fluorescence lifetime of the $6^1$ state with $\tau_e \approx 87(1)$ ns,[15] it was not possible to derive this assignment directly from the TRFD spectra. A numerical simulation of the RCS spectrum is shown below the experimental trace.[16] A rotational temperature $T_{\mathrm{rot}}$ in the range of 15−20 K has been assumed to reproduce the widths of the transients. The scaling factor between the modulation amplitude of the experiment and the simulation was ≈6. Figure 2 shows the results of a linear regression analysis including more than 80 transients. The interval of up to 8 ns delay contains 91 negative-going ground-state transients and 87 negative-going excited-state transients. The three empty regions have not been scanned because of the limited measurement time, resulting in an evaluation of about 50 % of the available transients. The regression residuals in Figure 2b show only small deviations that are mostly less than 1 ps. The time constants have been evaluated by a weighted least-squares fit with the uncertainties in the peak positions used as weights. The errors in the transient positions have been estimated by a fit of a Gaussian peak shape to individual transients. They are <1 ps for the ground-state and the excited-state transients. The linear regression analysis delivered $t_J'' = 43.9437 \pm 0.0022$ ps and $t_J' = 45.8719 \pm 0.0021$ ps. The rotational constants derived from these values are $B'' = 5689.10 \pm 0.28$ MHz (0.005%) and $B' = 5449.96 \pm 0.25$ MHz (0.005%). The errors given are estimated to represent uncertainties within a confidence interval of $2\sigma$.[17] From a comparison of the experimental transient intensities with simulated spectra we could also estimate an upper bound for the absolute value of the inertial defect $|\Delta I| < 0.13$ amu Å$^2$ for both electronic states (with $\Delta I = I_C - 2I_B$). This serves as a sensitive test for the planarity of benzene in both electronic states.[18] Moreover, these results are in excellent agreement with

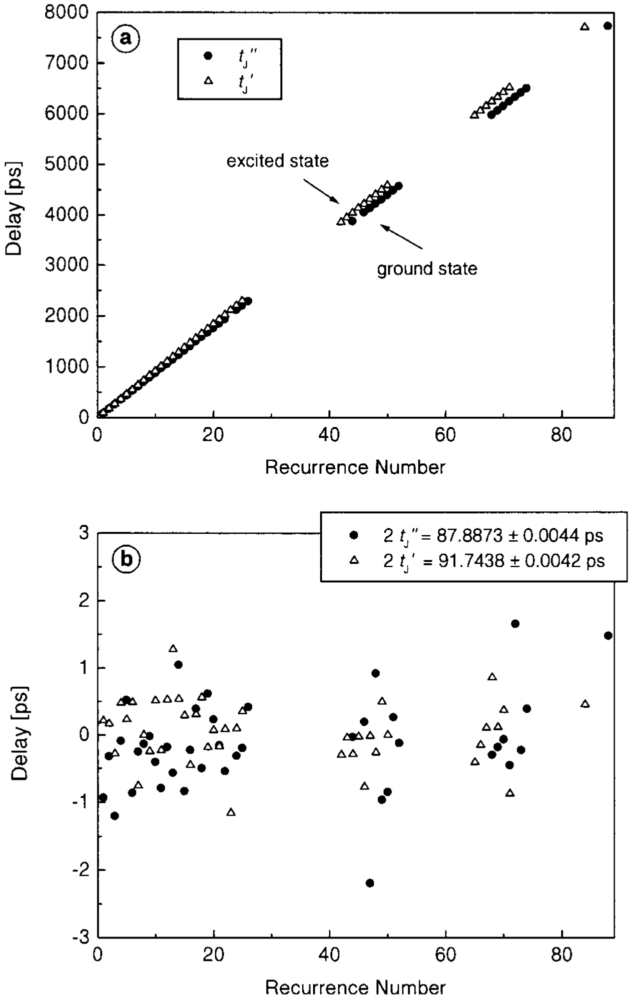

**Figure 2.** Linear regression analysis of the RCS spectrum of benzene. Evaluation of 41 $J''$ - (•) and 42 $J'$ - transients (Δ). (a) Straight-line fit: plot of delay time vs recurrence number n for the measured and identified transients. (b) Regression residuals.

the new high-resolution results obtained in the frequency domain, reporting $B'' = 5689.242 \pm 0.14$ MHz (0.002%) and $B' = 5449.976 \pm 0.13$ MHz (0.002%).[5] In addition to hydrogenated benzene ($C_6H_6$), the perdeuterated species ($C_6D_6$) also has been investigated by TRFD spectroscopy, showing the expected shift in the positions of the $J$-type transients of ≈9 ps/recurrence.

From these precise rotational constants, some structural implications, which are in line with the results of former frequency-resolved investigations, should be sketched in the following. First of all, the significant reduction of the rotational constant upon electronic excitation (of ≈4%) points toward a corresponding increase of the six-membered ring, which is consistent with the electronic $\pi-\pi^*$ transition reducing the bond order in the ring. Moreover, if one assumes $D_{6h}$ symmetry for both the ground and excited state, then there are only two bond distances, namely, C−C and C−H, necessary to describe the system. The application of the Kraitchmann equations utilizing our data for $C_6H_6$ and the isotopomeric results for $C_6D_6$ of ref 7 gave 1.3972 Å for C−C and 1.080 Å for C−H, both for the ground state. Upon electronic excitation a significant increase of the C−C bond length by +0.0353 Å and a smaller decrease of the C−H bond length by −0.015 Å was obtained. However, in this simple analysis, we have ignored the influence of the excitation of the $6^1$ in-plane deformation mode in the $S_1$ state. The excited-state rotational constant of benzene obtained on the $6_0^1 1_0^1$ band, i.e., with concurrent excitation of the symmetric breathing mode, shows a difference of −3.9 MHz with respect to the $6_0^1$ band.[6] This variation of 0.07% is well above the uncertainty of our RCS study. It is therefore possible to resolve the variation of the rotational constants between different vibronic levels by high-resolution RCS investigations. Hese and co-workers reported also the Coriolis coupling constants and accurate values for centrifugal distortion constants. These values are not available from a linear regression analysis of RCS transient positions. Significant higher order corrections are expected to broaden the transients asymmetrically and to reduce the modulation intensity of RCS recurrences. The magnitude of the centrifugal distortion constants is more than 6 orders of magnitudes smaller than that of the rotational constants.[5] It is therefore expected that its influence can be neglected in RCS experiments where the sample is kept at the low molecular beam rotational temperature. Experimental evidence for centrifugal distortion detected by RCS has been reported for smaller molecules, e.g., for $I_2$ at room temperature.[19,20] Recently, a degenerate four-wave mixing experiment (DFWM) with femtosecond pulses on $CHCl_3$ in a gas cell has been reported, where the rotational constant $B$ was determined with an estimated uncertainty of $5 \times 10^{-4}$ and the centrifugal distortion constant $D_j$ with an uncertainty of 1.5%.[21] Morgen et al.[22] estimated an uncertainty of $10^{-5}$ in the rotational constant of $O_2$ by evaluating a spectrum obtained with femtosecond Raman-induced polarization spectroscopy. Coriolis coupling constants and centrifugal distortion constants have not yet been included in the current implementation of our RCS simulation software.[13] Future results, especially with state-selective techniques,[23,24] will have to demonstrate how the sensitivity of high-resolution RCS with subject to these higher order terms compares with the results from rotationally resolved UV or IR spectroscopy.

In summary, we provide for the first time results of a RCS investigation of benzene. The experiments performed by TRFD were analyzed with a linear regression approach for the transient positions, and precise rotational constants with a relative uncertainty in the order of $10^{-5}$ for benzene for the ground and electronically excited states were obtained. The agreement with data from frequency-resolved experiments is excellent, although higher order (coupling) terms could not yet be determined. It has to be pointed out that benzene represents a favorable case for RCS experiments due to its long fluorescence lifetime of ≈87(1) ns[15] and high symmetry, resulting in persistent and relatively strong RCS transients (compared to benzene derivatives of lower symmetry). On the other hand, the *absolute* transient intensities (≈0.25%) and their widths (≈3.5 ps) are very small, both due to the relatively large value of the $B$ rotational constant. However, the presented results demonstrate the usefulness and precision of this time-resolved approach to determine structural data of aromatic systems.

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(16) Computer code for numerical RCS simulations, courtesy of P. M. Felker (UCLA).

(17) Not included in this evaluation is the actual accuracy of the delay line, which is now becoming significant, contributing up to 0.003% to the relative uncertainties. This uncertainty could be significantly reduced by an interferometric calibration of the delay line.

(18) A variation of $C$ from its assumed value of $B/2$ leads to a reduction in intensity of the transients at long time delay for the simulated spectra, because these transients are composed of $J$-, $K$-, and $C$-types. Since this was not observed experimentally, an upper bond for the inertial defect could be estimated.

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