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Rotationally Resolved ZEKE Photoelectron Spectrum of Benzene. Dynamic Jahn-Teller Effect in the $\nu_6(e_{2g})$ Mode

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The rotationally resolved zero-kinetic energy spectrum of benzene has been measured for ionization into the 6^1 level of the electronic ground state of benzene cation. Conclusive assignments have been given for the Jahn-Teller components j=1/2 and j=±3/2, arising from the linear and quadratic couplings.

The Jahn-Teller effect is one of the most important examples for the breakdown of the Born-Oppenheimer approximation. The benzene cation is a model system for Jahn-Teller induced perturbations and has attracted considerable interest, both theoretically and experimentally.1) However, up to now, no rotationally well-resolved spectrum has been reported allowing for a discussion of the Jahn-Teller effect in detail, especially concerning perturbations of the rotational structure of highly symmetric molecules.

The $\nu_6(e_g)$ mode is the lowest frequency Jahn-Teller active mode in the benzene cation.1) Photoelectron spectra of benzene measured by Long *et al.*2) suggested that the 6^1 band splits into j=3/2 and j=1/2 by about 300 cm^{-1}, where j is the half integer quantum number which replaces the vibrational angular momentum, l, and the electronic angular momentum $\Lambda(\pm 1)$.3) Very recently, Krause and Neusser4) measured a pulsed field ion spectrum in the region up to 800 cm^{-1} above the first ionization potential. They assigned the bands observed at 343, 363, and 674 cm^{-1} as j=-3/2, j=3/2, and j=1/2 of the 6^1 vibration, respectively. However, no rotational resolution was obtained in these measurements. In this paper it is shown that the measurement of rotationally resolved spectra is crucial for the assignment of these bands.

The first zero-kinetic-energy (ZEKE) photoelectron (PE) spectrum of benzene was measured by Chewter *et al.*,5) but the resolution of the reported spectra did not allow for an assignment on the basis of rotational quantum numbers. Recently we were able to improve the technique of ZEKE photoelectron spectroscopy to obtain rotationally well-resolved spectra even of big molecules like benzene.6) This enabled us to provide unambiguous assignments for the Jahn-Teller components of the 6^1 band of the benzene cation.

The experimental apparatus will be described in detail elsewhere.6) Briefly, the laser system consists of Nd:YAG laser (Continuum) pumped two dye lasers (Lumonics). The bandwidths of the two dye lasers are 0.05 cm^{-1} (FWHM) for the fundamental and about 0.09 cm^{-1} (FWHM) for the frequency doubled light. The first laser pumps a specific rotational level in the $S_1\ 6^1$ state. The second laser promotes the molecule into long-lived Rydberg states close to the ground state cation. After a delay of 3 µs, an extraction step pulse6,7) was applied by

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using an arbitrary function generator (Le Croy 9100). The time-of-light electrons were detected using multichannel plates. The signal was recorded with a transient digitiser by setting narrow gates (10 – 15 ns).

Figure 1 shows the selection of the rotational states in S_1 in the (1+1) one-color, two-photon ionization spectrum via the $S_1\,{}^1B_{2u} \leftarrow S_0\,{}^1A_{1g}\ 6^1_0$ transition. A comparison of Fig. 1 with a high-resolution (FWHM=0.004 cm^{-1}) sub-Doppler fluorescence excitation spectrum measured by Riedle *et al.*[6] predicts that the ${}^rR_0(0)$ transition marked with A is populated in a single rovibronic state (J'=1, K'=1). We measured the ZEKE-PE spectrum by fixing the first dye laser at the peak position of A ($\tilde{\nu}$ = 38606.52 cm^{-1}), and scanning the second dye laser. A typical ZEKE-PE spectrum in the region $\tilde{\nu}$ = 36290 – 36330 cm^{-1} is shown in Fig. 2. As is clear from this figure, the rotational structure in the two vibronic transitions are almost identical. The $6^1(e_{2g})$ level in the ${}^2E_{1g}$ electronic ground state will split into the $B_{1g} \oplus B_{2g}$ and E_{1g} states by the linear dynamic Jahn-Teller effect.[1] The $B_{1g} \oplus B_{2g}$ state will further split into the B_{1g} and B_{2g} states due to the quadratic dynamic Jahn-Teller effect.[9] The rotational structure of the two vibronic transitions arising from the quadratic Jahn-Teller effect is expected to be very similar, because both the states belong to the same symmetry species B, and the rotational constants for the two states should be nearly the same. These considerations are consistent with the observation of almost identical rotational structure in Fig. 2. Thus we conclude that the lower and higher components detected in Fig. 2 are 6^1(j=-3/2) and 6^1(j=3/2), respectively.

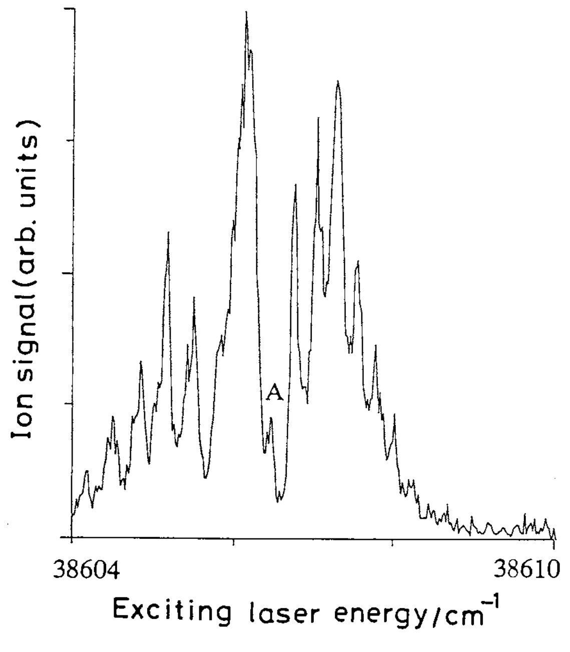

Fig. 1. One-color, two-photon REMPI spectrum of benzene via the $S_1\,{}^1B_{2u} \leftarrow S_0\,{}^1A_{1g}\ 6^1_0$ transition. The peak marked with A corresponds to the ${}^rR_0(0)$ transition in one single rovibronic state (J'=1, K'=1) excited in the intermediate state.

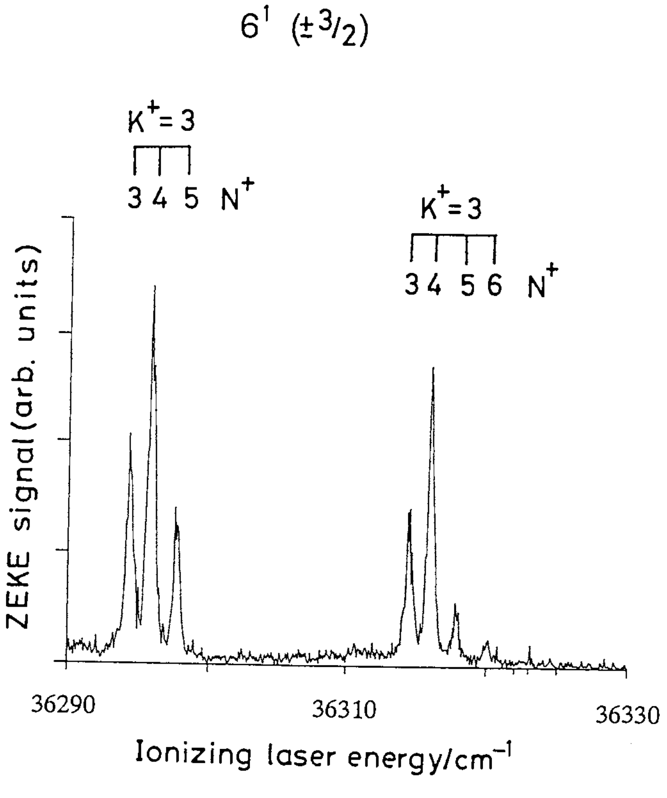

Fig. 2. ZEKE spectrum into 6^1 (j=±3/2) state of the electronic ground state of the benzene cation via peak $S_1 6^1$ (J'=1, K'=1).

Each rotational state (denoted $N^+_{K^+}$) is characterized with N^+, denoting the total angular momentum quantum number, excluding electronic spin, and with projection quantum number K^+.[10,11] We gave assignments by using a similar procedure as is the case for the assignments of the ZEKE-PE spectra of ammonia[10] and benzene.[6] It has been found that the separation of two transitions with the same quantum numbers N^+ and K^+ is identical within the accuracy of ±0.1 cm^{-1}. The average splitting of the j=-3/2 and j=3/2 levels has been determined to be 20.1 cm^{-1}, which is in good agreement with the splitting measured by Krause and Neusser[4] from the bandhead positions.

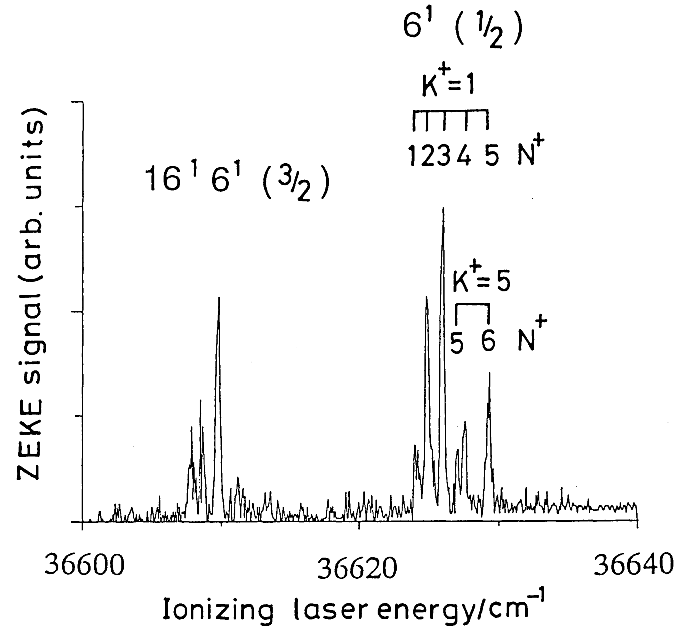

Fig. 3. ZEKE spectrum into the $16^1 6^1$ (j=3/2) and 6^1 (j=1/2) states of the electronic ground state of the benzene cation via $S_1 6^1$ (J'=1, K'=1).

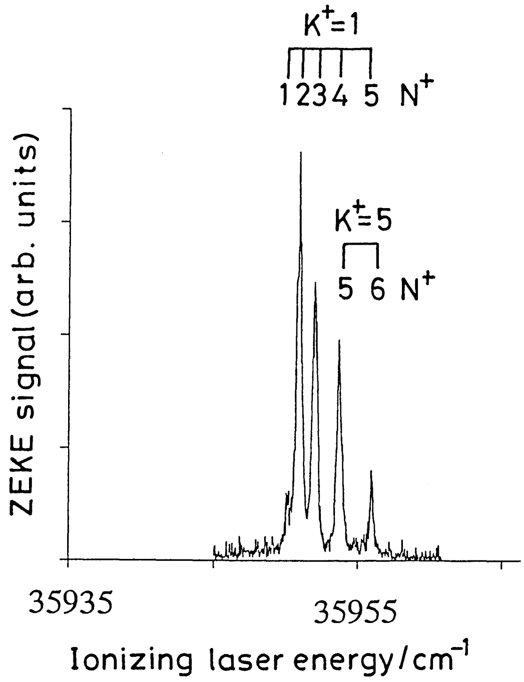

Fig. 4. ZEKE spectrum into the vibrationless electronic ground state of the benzene cation via $S_1 6^1$ (J'=1, K'=1) [from Ref. 6, with permission].

The ZEKE-PE spectrum in the region $\tilde{\nu}$ = 36600 – 36640 cm^{-1} is shown in Fig. 3. Two vibronic transitions are observed in this region. Kraus and Neusser[4] assigned the lower state as $16^1 6^1$(j=3/2) and the higher state as 6^1(j=1/2). It should be noted that the 6^1(j=1/2) state has the same vibronic symmetry species E_{1g} as the vibrationless ground state of the benzene cation D_0 E_{1g}. Thus the rotational structure of the two states should be similar, except for slightly different rotational constants and different Coriolis coupling parameters. Figure 4 shows the ZEKE-PE spectrum of the transition into the vibrationless ground state D_0 of the cation,[6] starting from the same intermediate state as for the spectra in Figs. 2 and 3. Obviously, the structure of the higher state in Fig. 3 is similar to that of the ground state (Fig. 4). In contrast, the rotational structure of the lower state in Fig. 3 is fairly different. We therefore conclude that the higher state in Fig. 3 is 6^1(j=1/2) on the basis of the rotational assignment. This is consistent with the assignment given by Krause and Neusser.[4] The rotational structure of the lower state in Fig. 3 is consistent with the rotational structure of the combination mode $16^1 6^1$(j=3/2).[12)]

The splittings between the bands with the same quantum number N^+ (but different K^+) of j=+3/2 or j=-3/2 and j=1/2 (i.e. between 3_3 of j=-3/2 or 3_3 of j=+3/2 and j=1/2) has been measured to be 311.9 and 331.9 cm^{-1}, respectively. In order to obtain the values of the splittings between the origin positions of the j=3/2 and j=1/2 levels, a precise determination of the rotational constants from the measurement of ZEKE spectra, ionizing from various intermediate vibronic states, is necessary.

In summary, very high-resolution rotationally resolved ZEKE-PE spectra of benzene have been measured. The j=±3/2 and j=1/2 Jahn-Teller components of the 6^1 state of the cation have been assigned unambiguously. The Jahn-Teller splittings obtained in this work are important for the test of the validity of the theory. Very high-resolution ZEKE-PE spectroscopy promises to solve unknown problems in large molecular ions.

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