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Infrared Spectroscopy of Neutral C_7H_7 Isomers: Benzyl and Tropyl

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Small monocyclic alkyl-substituted molecules present prototypical systems to study ring expansion isomerization reactions. Fundamental insight into the structure of the reactants and products as well as into the reaction paths connecting the isomers can be obtained when these species are studied in the gas phase, in which the molecules are isolated from external influences.

An intensely studied example is the isomerization reaction from toluene to 1,3,5-cycloheptatriene in the cationic state.[1] Losing one hydrogen atom from the latter ion can yield the tropyl cation, often dubbed "tropylium" (systematic name for the neutral radical: cycloheptatrienyl). It has been proposed that isomerization between cationic tropyl and benzyl[2] as well as isomerization between the neutral radicals of these species[3] follow similar pathways. Tropylium is an exotic member of the family of aromatic molecules, as it exhibits its aromicity as a cation. The molecule has an unusual seven-fold rotation axis and belongs to the point group D_{7h}. Neutral and cationic tropyl have been the focus of several studies, both theoretical and experimental.[3−5]

Another very stable $C_7H_7^+$ isomer is the benzyl cation. There has been much debate about which of the two C_7H_7 cations is lower in energy as well as about the height of the barrier for isomerization. It is generally agreed upon by now that the tropyl cation is the more stable isomer by about 0.24 eV,[6] and the isomerization barrier for the reaction from the tropyl cation to the benzyl cation has recently been calculated to be about 3 eV.[2] In the neutral species, the benzyl radical is more stable than the tropyl radical by about 0.73 eV.[7] In the neutral tropyl radical an unpaired electron in a degenerate orbital is present, giving rise to a vibronic interaction, the Jahn−Teller (JT) effect.[8] This coupling between electronic motion and vibrational motion causes the molecule to distort from the symmetrical configuration. In the case of the JT-distorted benzene cation, the zero-point energy is above the conical intersection, leading to an effective D_{6h} structure.[9] In fact, ESR data suggest that the effective structure of tropyl is the symmetrical D_{7h} structure.[10] Fundamental insight into the structure of such species can be obtained by recording their vibrational properties, using for example infrared (IR) spectroscopy.[11] Here, we report on the first gas-phase IR absorption spectrum of both the benzyl and the tropyl radical in the 400−1800 cm^{-1} spectral region.

The IR spectra of the C_7H_7 isomers are measured by using an IR−UV double resonance scheme that has been described previously.[12] To generate the benzyl radical, benzyl chloride (Fluka, 99%) is used as a precursor. The benzyl chloride is allowed to evaporate, mixed with argon at 3 bar, and injected into the vacuum chamber using a pulsed valve. About 3 mm in front of the valve, a ring electrode is mounted to which a voltage between −500 and −1000 V is applied. When the valve opens, the pressure rises momentarily and electrical breakdown occurs. In such a discharge source, molecules can be energized, fragmented, isomerized, and possibly ionized.[13] Specifically, after breaking the C−Cl bond of benzyl chloride, the benzyl radical is formed. The radicals are cooled in the expansion, and a molecular beam is produced. Further downstream, the beam is skimmed upon entering the chamber where it interacts with the infrared beam of the free electron laser "FELIX" [14] as well as with the output of a UV laser. When FELIX is resonant with an IR active vibration of the radical, the ground-state population is depleted. After the infrared pulse, the UV laser pulse probes the amount of benzyl radicals that remains in the ground state. The frequency of the UV laser is set to be resonant with the $D_3 \leftarrow D_0$ transition of benzyl at 32760 cm^{-1}.[3] A second photon of the same frequency ionizes the radical, allowing for time-of-flight mass spectrometric detection. By monitoring the ion current at 91 amu as a function of FELIX wavelength, the IR spectrum of the radical can be recorded.

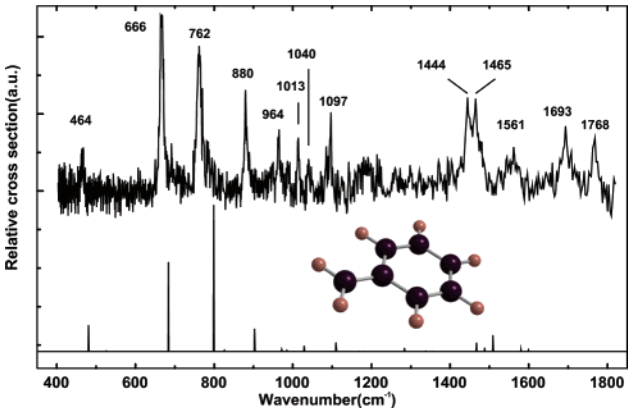

Figure 1. Infrared absorption spectrum of the benzyl radical ($C_6H_5CH_2$) (upper trace). In the lower trace a stick spectrum obtained from quantum chemical calculations is shown.

For the tropyl radical the same procedure is used. Cycloheptatriene is now used as a precursor; abstraction of a hydrogen atom in the discharge leads to the formation of the tropyl radical. The excitation frequency that is used in the 1+1 ionization scheme corresponds to the $D_1(2_0^1) \leftarrow D_0(0_0^0)$ transition at 26573 cm^{-1}.[3]

The experimental infrared spectrum of the benzyl radical in the D_0 state is shown in Figure 1 as the upper trace. The lower trace shows a stick spectrum obtained from an ab initio calculation at the B3LYP/D95(d,p) level.[15] Not shown are two calculated modes at 202 and 356 cm^{-1}, which are predicted to have low IR intensity, and which are outside the measured frequency range. The experimental spectrum contains at least 13 identifiable resonances, and their positions, together with the calculated frequencies and intensities, are given as Supporting Information.

The main features seen in the experimental spectrum are well reproduced by the calculation. The actual frequency shift from the observed modes to the calculated modes is on the order of +3%. A somewhat larger shift is observed for the mode at 762 cm^{-1}, which is assigned to the mode calculated at 799 cm^{-1}. The calculation shows that this mode involves a large amount of out-

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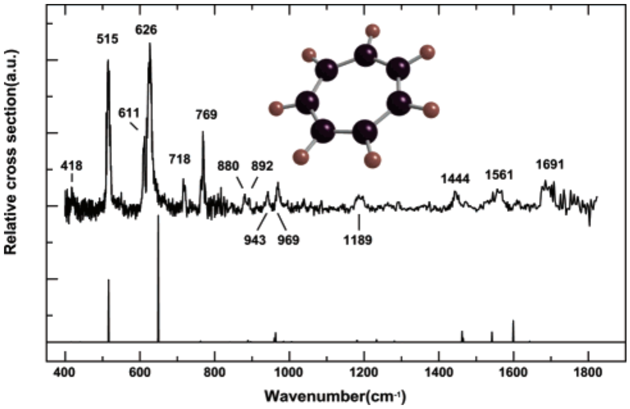

Figure 2. Infrared spectrum of the tropyl radical (C_7H_7). A stick spectrum obtained from a quantum chemical calculation is shown as the lower trace.

of-plane motion of the H-atoms of the $-CH_2$ group. It might well be that the potential along this coordinate is more anharmonic, which would explain why theory fails to accurately predict position and intensity of this mode.

Below 1000 cm^{-1}, the calculated fundamental IR-active modes almost exclusively involve C−H out-of-plane bending motion. Above 1000 cm^{-1}, the calculated IR-active modes mainly involve in-plane motion. The mode calculated at 1510 cm^{-1} is one of the few modes that is dominated by motion in the CH_2 group and corresponds to a CH_2 “scissors”-mode. The peak experimentally observed at 1465 cm^{-1} most likely corresponds to this localized CH_2 “scissors” mode.

No fundamental modes are calculated between 1600 and 3000 cm^{-1}. The transitions observed beyond 1600 cm^{-1} most likely originate from combination bands. Such bands possibly occur in other parts of the spectrum as well. The infrared spectrum of the benzyl radical has also been measured by using matrix isolation spectroscopy (MIS) in an argon matrix at 12 K.[16] Most of the observed MIS bands correspond to bands observed in the current experiment to within a few cm^{-1}. Compared to the MIS data we observe additional weak bands in the region around 1000 cm^{-1} and beyond 1500 cm^{-1} as shown in the Supporting Information. Additional information on the vibrational structure of the benzyl radical has been obtained by using fluorescence spectroscopy (see Supporting Information).[17]

The infrared spectrum of the other C_7H_7 isomer, tropyl, is shown in Figure 2 as the upper trace. The infrared spectrum shows at least 14 distinct resonances, with dominant features at low frequencies. The JT effect will cause the tropyl radical to distort on the D_e surface from D_{7h} to C_{2v}. The inclusion of zero-point energy, however, might cause the molecule to effectively remain of D_{7h} symmetry. In the ab initio calculation at the B3LYP/D95(d,p) level (see lower trace of Figure 2), only the static distorted C_{2v} structure is considered. A much better approach would be to correctly treat the JT effect in D_{7h} symmetry, similar to approaches used for the benzene cation,[18,19] but this is beyond the scope of the present work.

The two strong low-frequency resonances that are calculated at 516 and 649 cm^{-1} are exclusively C−H out-of-plane bending motions. The mode at 889 cm^{-1} and all higher-frequency IR active modes involve exclusively in-plane motion. While the JT effect mainly has an impact on in-plane modes, the perturbation on the out-of-plane modes is expected to be small, and thus these modes should be well modeled by the quantum chemical calculation. Indeed, in agreement with the calculation, two modes are observed at 515 and 626 cm^{-1}. Theory, however, fails to predict most of the other modes.

It can be noted that significantly more modes than predicted by the simple theory are observed experimentally. Specifically at low frequencies, relatively strong modes are observed at 611, 718, and 769 cm^{-1} that have no counterpart in the calculated spectrum.

It is thus of interest to examine the influence of the JT effect on the experimental spectrum. The symmetries of the JT active modes in the X^2E_2'' electronic ground state are e_3'(linearly JT active) and e_2', e_2''(quadratically JT active). Modes of these symmetries will split and shift, sometimes up to several hundreds of wavenumbers, away from the unperturbed positions.[19] Since split modes of e_3' and e_2' symmetry have a component that corresponds to a dipole allowed transition in C_{2v}, they are expected to appear in the IR absorption spectrum.

Therefore, to unravel the spectrum, a detailed analysis that correctly takes into account the JT effect has to be done, and the here presented experimental spectrum can serve as a benchmark to understand the JT effect in this interesting species.

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Supporting Information Available: Tables containing the calculated vibrational frequencies and intensities for the tropyl and the benzyl radical along with experimentally observed resonances (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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