Infrared Spectroscopy of Neutral C$_7$H$_7$ Isomers: Benzyl and Tropyl

Rob G. Satink,∗† Gerard Meijer,‡‡ and Gert von Helden¶

FOM-Institute for Plasma Physics “Rijnhuizen”, Edisonlaan 14, NL-3439 MN, Nieuwegein, The Netherlands, and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

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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 of the molecules are isolated from external influences.

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Fundamental insight into the structure of the reactants and products can be obtained by recording their vibrational properties, using for example infrared (IR) spectroscopy.¹¹ Here, we report on the first 1 spectral region.

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$_0^+$) ← D$_0$(0$_0^+$) transition at 26573 cm$^{-1}$.¹³

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 corresponds to the D$_1$(2$_0^+$) ← D$_0$(0$_0^+$) transition at 26573 cm$^{-1}$.¹³

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 that are outside the measured frequency range. The experimental spectrum contains at least 13 identifiable resonances, and which are outside the measured frequency range. The experimental spectrum contains at least 13 identifiable resonances, and which are outside the measured frequency range.

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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-
of-plane motion of the H-atoms of the −CH 3 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 3 group and corresponds to a CH 3 “scissors”-mode. The peak experimentally observed at 1465 cm −1 most likely corresponds to this localized CH 3 “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 7 H 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 1 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 1 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 2 E 2 electronic ground state are ε 1′ (linearly JT active) and ε 2′, ε 3′ (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 ε 1′ and ε 3′ 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.

References

(7) Calculated from the ionization potential (IP) of tropyl (ref 4), the IP of benzyl (Eiden, G. C.; Weinhold, F.; Weisshaar, J. C. J. Chem. Phys. 1991, 95, 8665) and the difference in heat of formation of the cationic radicals (ref 6).

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Figure 2. Infrared spectrum of the tropyl radical (C2H7). A stick spectrum obtained from a quantum chemical calculation is shown as the lower trace.