**Triplet Naphthyl Cation**

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# Spectroscopic Evidence for a Triplet Ground State in the Naphthyl Cation**

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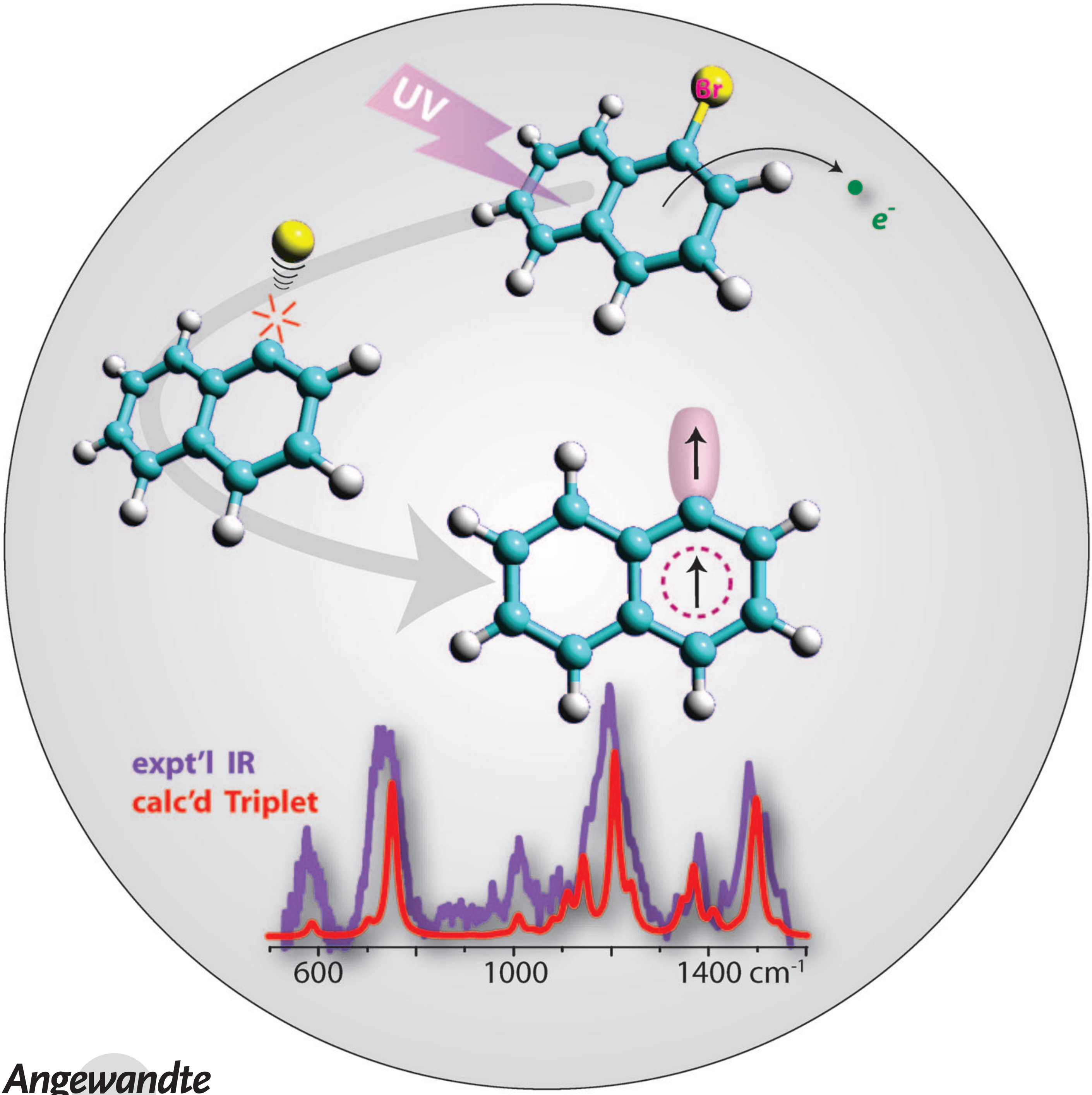

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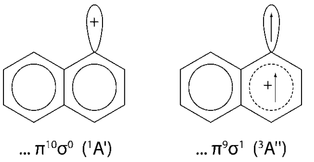
Carbocations play an essential role as intermediates in organic chemistry,[1] yet their high reactivity challenges determination of their physical and chemical properties.[2] Aryl cations form an important class of carbocations and the character of the ground electronic state of the phenyl cation ($C_6H_5^+$) has long been subject of debate,[3–11] illustrating these challenges. The empty $\sigma$-orbital on the C$^+$ atom[5] induces sp hybridization causing a substantial deformation of the hexagonal frame. Transfer of an electron from the $\pi$-system to the empty $\sigma$-orbital[6] restores the sp$^2$ hybridization at the cost of forming a triplet ($^3B_1$) electronic state and sacrificing the aromaticity of the system.[4] By now, a singlet ($^1A_1$) ground state about 77 kJ mol$^{-1}$ lower in energy than the triplet has been firmly established.[7]

Electron-donating substituents as well as an increased $\pi$-system reduce the energy required to remove a $\pi$-electron, decreasing the energy gap between triplet and singlet states.[12–14] For the naphthyl cation ($C_{10}H_7^+$, Scheme 1) both states are close in energy at the density functional theory (DFT) level,[12,15,16] although other methods place the triplet either notably lower[17,18] or higher.[15,19] The observed reactivity of naphthyl$^+$ in solution was interpreted as resulting from a singlet-state cation.[16] Electron donation of solvent molecules into the vacant $\sigma$-orbital stabilizes the singlet relative to the triplet, which is indeed borne out by DFT calculations.[16] Gas-phase studies are thus required to evaluate the intrinsic stability of both spin states and while various mass-spectrometric studies on $C_{10}H_7^+$ have been reported,[15,20,21] they do not probe its (electronic) structure.



***Scheme 1.*** The 1-naphthyl cation $C_{10}H_7^+$ in its singlet (left) and triplet (right) electronic configurations.

Spectroscopy of the gas-phase ion could directly reveal its structure. A gas-phase IR spectrum was recently reported for the phenyl cation[22] by Ar-tagging photodissociation spectroscopy.[23,24] Although rare-gas tagging is considered to induce negligible perturbations to the system under study, this is not the case for aryl carbocations, where the in-plane binding of the Ar atom to the C$^+$ center results in substantial electron donation into the vacant $\sigma$-orbital.[22] In order to determine the ground state of the isolated naphthyl cation, such a strategy might thus artificially enhance the stability of the singlet state. Instead, we employ here IR multiple photon dissociation (IRMPD) spectroscopy of bare naphthyl$^+$ isolated in a quadrupole ion trap.

Figure 1 shows the equilibrium geometries for the singlet and triplet minima of the 1- and 2-naphthyl$^+$ isomers, which are of $C_s$-symmetry except for singlet 2-naphthyl$^+$, which optimizes to a non-planar $C_1$ geometry.[16,19] The singlet ($^1A'$) and triplet ($^3A''$) structures for each of the isomers are found to be virtually iso-energetic. Independent of the electronic state, the 2-naphthyl cation is about 5.4 kJ mol$^{-1}$ higher in energy than the 1-isomer.

The carbon frame of the singlet structures is significantly distorted from the naphthalene $D_{2h}$ geometry. The CC$^+$C angle amounts to 149°, reflecting the tendency to form a linear CC$^+$C bond typical for an sp-hybridized carbon atom.[13] In the triplet state, the angle becomes 127°, close to the hexagonal 120° angle, as a consequence of the restored sp$^2$ hybridization due to the $\pi$-electron transferred to the empty $\sigma$-orbital. As compared to $C_6H_5^+$, the larger $\pi$-system in $C_{10}H_7^+$ makes removal of a $\pi$-electron more facile so that the energetic penalties for geometry distortion (singlet) and formation of a bi-radical (triplet) become competitive.

IRMPD spectra of $C_{10}H_7^+$ obtained with 1- and 2-bromonaphthalene isomers as precursor are identical (see Supporting Information) and the experimental spectrum shown in the top panel of Figure 1 represents an average of several runs. Likely, isomerization to the more stable 1-naphthyl$^+$ occurs when 2-bromonaphthalene is used. Isomerization by a 1,2-hydride shift is indeed expected to be efficient as the 3-center-2-electron transition state in carbocations is aromatic[25] and was in fact suggested to explain the observed reactivity in solution.[16] Computed spectra for singlet and triplet states of both naphthyl$^+$ isomers are also shown in Figure 1. Clearly, the 1-naphthyl$^+$ triplet spectrum matches the experimental data better than any of the other computed spectra, although the spectra of both triplet state isomers are sufficiently similar to not rule out the presence of any triplet 2-naphthyl$^+$. Nonetheless, regardless of the isomer, triplet naphthyl$^+$ clearly dominates over singlet naphthyl$^+$. Table 1 lists experimental and calculated band positions for the $^3A''$-1-naphthyl ion confirming the good agreement.

The observation of a triplet state may reflect its lower energy relative to the singlet state, but propensities in the formation of the naphthyl cation should also be considered. Firstly, the relative energies of the two states as predicted by DFT may not be accurate. Values for the singlet–triplet energy gap obtained using other computational methods indeed show significant scatter, favoring the triplet state (PM3,[17] CISD, ROHF,[18] HF[19]) or the singlet state (MP2,[19] CCSD(T)[15]) by substantial amounts. This result suggests that a multireference approach as has been applied to the phenyl[7]

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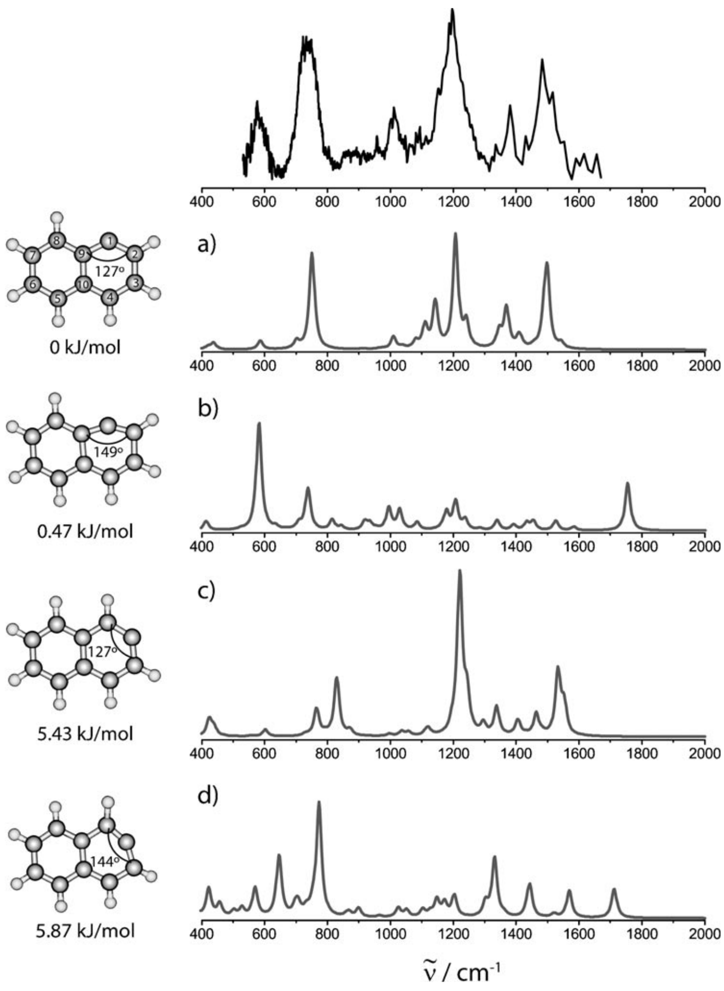

***Figure 1.*** Experimental IR spectrum of the $C_{10}H_7^+$ carbocation (top) compared to theoretical spectra of triplet 1-naphthyl$^+$ (a), singlet 1-naphthyl$^+$ (b), triplet 2-naphthyl$^+$ (c), and singlet 2-naphthyl$^+$ (d). The strongest IRMPD feature near 1196 $cm^{-1}$ consists of four convoluted bands calculated at 1110, 1143, 1207 and 1241 $cm^{-1}$ for triplet 1-naphthyl$^+$, characterized mainly by CH in-plane bending vibrations involving some CC-stretching character as well. The relative intensities of the bands observed at 1011 and 580 $cm^{-1}$ appear larger than what is predicted for triplet 1-naphthyl$^+$, perhaps reflecting a small contribution of singlet 1-naphthyl$^+$, which features predicted absorptions around 1000 $cm^{-1}$ and at 584 $cm^{-1}$. It is important to note, however, that relative intensities may not be accurately reproduced by our spectroscopic method, which is based on the absorption of multiple photons,[26] and that calculated absorption cross-sections may be less reliable. Nonetheless, the overall comparison between measured and calculated spectra clearly suggests that triplet naphthyl$^+$ dominates the ion population.

and vinyl[13] cations may be required in this case as well. On the other hand, the study on substituted vinyl cations found good agreement between DFT and CASPT2 values for the singlet–triplet gap,[13] encouraging the use of low-cost DFT methods.

It may be wondered whether there are propensities that preferentially form one of the two electronic states in the C–Br bond cleavage. For instance, formation of the phenyl cation from the neutral $C_6H_5^{\cdot}$ radical by photoionization favors the higher-energy triplet state due to better Franck–Condon overlap.[7] Analogously, homolytic bond cleavage in the $C_{10}H_7Br^+$ radical cation would lead to the triplet naphthyl cation. However, most gas-phase reactivity studies involving the naphthyl cation have largely ignored possible implications of the different spin states[20,21] or simply assumed both states to occur.[15] Moreover, H-atom abstraction (HAA) from the benzene cation was first assumed to produce the (higher-energy) triplet phenyl cation,[27] but later studies suggested that an intersystem crossing occurs on the dissociation pathway, rapidly converting the system to the (lower-energy) singlet state.[6] Spin isomerization between singlet and triplet states has also been suggested to occur rapidly for a series of *para*-substituted phenyl cations, *p*-X-$C_6H_4^+$, such that the lower-energy state is always found independent of how the species was formed.[28] This rapid spin conversion is induced by the low minimum energy crossing point (MECP) connecting the two electronic surfaces and the non-negligible spin-orbit coupling (SOC) constants.[28] Assuming that the additional ring in the naphthyl cation behaves as an electron-donating substituent,[12,16] rapid spin relaxation is expected to occur here as well. The unambiguous assignment of the IR spectrum in Figure 1 then suggests a triplet electronic ground state for the naphthyl cation.

In conclusion, the IR spectrum of the gaseous naphthyl cation, $C_{10}H_7^+$, was recorded by IRMPD spectroscopy, providing the first experimental spectrum of an isolated, bare aryl cation. Comparison of the experimental spectrum with spectra calculated for singlet and triplet naphthyl$^+$ shows that a triplet-state ion is predominantly formed. In general, this study shows that changes in the electronic structure induce geometric changes that can be clearly distinguished in IR spectra. DFT calculations predict the triplet state to be further stabilized relative to the singlet state for larger aryl cations, which we currently investigate experimentally.

## *Experimental Section*

The experimental setup consists of a Paul-type ion trap with a time-of-flight (TOF) mass spectrometer, coupled to the free electron laser for infrared experiments[29] (FELIX).[26] The naphthyl cation ($C_{10}H_7^+$) is generated by ArF laser photoionization of bromonaphthalene ($C_{10}H_7Br$) vapor and concomitant relaxation by C–Br bond cleavage. The appearance energy of $C_{10}H_7^+$ is about 12 eV,[20] so that the absorption of two 193 nm photons provides sufficient energy. Both 1- and 2-bromonaphthalene isomers were used as precursor. Resonant irradiation of $C_{10}H_7^+$ with a single 50 mJ pulse of FELIX induces loss of a $C_2H_2$ unit, which is monitored in the TOF-MS. The yield of fragment ions is recorded as the IR frequency is scanned from 500 to 1700 $cm^{-1}$, giving the IRMPD spectrum of $C_{10}H_7^+$.

Formation of singlet and triplet $C_{10}H_7^+$ by homolytic C–Br bond cleavage are both spin allowed. Previous DFT studies suggest both states to be very close in energy.[12,16] Herein we use B3LYP/6-311++G(d,p) in Gaussian03 to optimize singlet and triplet states for 1- and 2-naphthyl[30] cation isomers and to compute harmonic vibrational frequencies. No imaginary frequencies were found. Stick spectra are

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***Table 1:*** Comparison of observed and computed IR absorption bands.

| Expt freq[a] | Theory freq[a,b] | int[c,d] | $C_s$ | description[e] |
|---|---|---|---|---|
| 580 | 586 | 10 | A“ | ring oop deformation |
| 735 | 750 | 98 | A“ | CH oop bend |
| 1011 | 1010 | 14 | A′ | CH ip bend/ring breathing |
| 1196 | 1110 | 29 | A′ | CH ip bend/ring deform |
| | 1143 | 52 | A′ | CH ip bend |
| | 1207 | 118 | A′ | CH ip bend/CC stretch |
| | 1241 | 35 | A′ | CH ip bend/CC stretch |
| 1380 | 1347 | 25 | A′ | CH ip bend/ring deform |
| | 1369 | 46 | A′ | CC stretch/CH ip bend |
| | 1408 | 18 | A′ | CH ip bend |
| 1485 | 1497 | 88 | A′ | CC stretch/CH ip bend |

[a] In cm$^{-1}$ [b] For triplet 1-naphthyl$^{+}$. [c] In km mol$^{-1}$ [d] Only bands with intensities $>12$ km mol$^{-1}$ included (except 585 cm$^{-1}$ band). [e] mode description: ip = in plane; oop = out of plane.

convoluted with a 20 cm$^{-1}$ full width at half maximum (fwhm) Lorentzian function.

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[30] 1- and 2-naphthyl isomers are also often referred to as α- and β-naphthyl, respectively.

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