Electronic Spectrum of Dihydrogenated Buckminsterfullerene in a 6 K Neon Matrix

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Vibrationally resolved electronic absorption spectrum of 1,2-dihydrogenated[60]fullerene has been recorded in a 6 K neon matrix after mass-selected deposition of m/z = 722 cations produced from reaction of protonated methane and C_{60} in an ion source. One system has the origin band at 688.5 ± 0.1 nm and another commencing at 404.8 ± 0.1 nm. Theoretical computations were used to calculate the relative energies of three isomers of dihydrogenated[60]fullerene and time-dependent density functional theory predicted the vertical excitations to 50 electronic states.

Fullerenes are spherical or ellipsoidal structures of pure carbon, such as C_{60}, C_{70}, and C_{84}. These molecular geometries are the smaller counterparts of extended carboneous nanotubes. C_{60} is the most stable fullerene and was first generated more than 30 years ago in the laboratory by laser vaporization.[1] It has also been suggested that fullerenes form around stars with carbon-rich atmospheres and hydrogen-poor stellar environments.[2–5] Hydrogenated amorphous carbon grains in the interstellar medium (ISM) may decompose from shock waves into polycyclic aromatic hydrocarbons (PAHs) and fullerenic species;[6] PAHs may comprise ≈ 20 % of carbon-containing compounds in space.[7,8]

Buckminsterfullerene C_{60} was first detected in a young planetary[9] and reflection nebula.[10] However, given the significant photon flux below the hydrogen Lyman α energy, neutral C_{60} present in the diffuse ISM would be ionized, being predicted first by Kroto.[11] Recently, it has been shown that C_{60}^+ is the carrier of five astronomical absorption features, known as diffuse interstellar bands (DIBs).[12–15] It has also been suggested that C_{60}^+ may undergo ion-neutral reactions with atomic hydrogen,[2] making $C_{60}H_n^+$ ($n > 1$) cations possible species in the ISM. These types of protonated species could also be candidate molecules for the DIBs observed towards reddened stars. Another ion-neutral reaction that would produce $C_{60}H_2^+$ is $C_{60} + H_3^+ \rightarrow C_{60}H^+ + H_2$, and recombing with free electrons, the reaction $C_{60}H + H_3^+ \rightarrow C_{60}H_2^+ + H_2$ can proceed. Hydrogenated fullerenes, $C_{60}H_n$, could be created in the diffuse ISM over billions of years; however, this is dependent on the electron capture and ionization rates.

UV/Vis spectra were measured before in the liquid-phase of $C_{60}H_n$ $n = 2,4$ to determine if the desired synthesis was completed. In the condensed phase, two distinct absorptions are present for $C_{60}H_2$ at 710 and 435 nm.[16] In this contribution, a vibrationally well-resolved electronic spectrum of $C_{60}H_2$ was measured in a 6 K neon matrix and vertical excitation energies were calculated to assist an assignment. Mass-selective deposition of $C_{60}H_2^+$ was undertaken; however, electron recombination occurred with cations in the crystalline neon and only neutral $C_{60}H_2$ was observed.

Methods

Experimental.—The setup for mass-selected matrix isolation of ions is described elsewhere.[17] Buckminsterfullerene C_{60} vapor was generated by heating the sample to ca. 650 K. Cations, predominately $C_{60}H_n^+$ $n > 1$ were produced in a hot cathode discharge source from C_{60} diluted in gaseous methane. Ions were extracted and guided

through an electrostatic bender to a quadrupole mass selector (QMS). Ions of m/z = 722 passed through the QMS and were codeposited with a mixture of neon and CH3Cl (20 000:1) onto a rhodium-coated sapphire plate at 6 K. CH_3Cl acts as an electron scavenger, creating Cl^- by dissociative electron attachment and compensating the positive charge. After a ≈ 150 μm thick matrix was produced, electronic absorption spectra were measured in the 280−1100 nm range by passing broadband radiation through crystalline neon, parallel to the matrix substrate. Light was wavelength-dispersed by a 0.3 m spectrograph and detected with a CCD camera. A photobleaching procedure was employed to distinguish absorptions of cations from those of neutrals. The neon matrix was irradiated with UV light from a medium pressure mercury lamp. Electrons are detached from Cl^- and neutralize positively charged species. Absorptions which decrease upon UV irradiation have a cationic origin, whereas those which increase in intensity are due to neutral molecules.

Computational.—Equilibrium structures for different isomers of $C_{60}H_2$ were calculated with density functional theory (DFT) using B3LYP functional[18,19] and cc-pVDZ basis set.[20] Computations were carried out with the Gaussian 09 program package.[21] Vertical excitation energies of the species (all with C_1 symmetry) were calculated with time dependent (TD-DFT) to compare experimental and theoretical values.

Results and Discussion

The electronic spectrum of 1,2- dihydrogenated[60]fullerene (1,2-$C_{60}H_2$) in a 6 K neon matrix is illustrated in Figures 1 and 2. There is one system that has absorptions around 690 nm and another one beginning at 410 nm. The bands in the near-UV are from a number of electronic transitions and state-to-state mixing makes for a difficult assignment.

The first dipole-allowed electronic transition (Figure 1) has an origin band maximum at 688.5 ± 0.1 nm (14 524 cm^{-1}). There is a second absorption in a 6 K neon matrix at 677.0 nm (14 771 cm^{-1}), blueshifted to the origin band by 247 cm^{-1}. This vibration is most likely a fullerenic breathing mode, involving the carbon cage-structure of the whole molecule. In the liquid-phase,[16] the maximum is redshifted relative to solid-neon by ca. 20 nm. This is due to solvent and temperature effects, because the measurement was taken at 298 K. Upon photobleaching the matrix, the two bands at 688.5 and 677.0 nm gain intensity (Figure 1, red), concluding that the carrier is neutral. If these were to decrease in overall intensity, they would be from a cationic species.
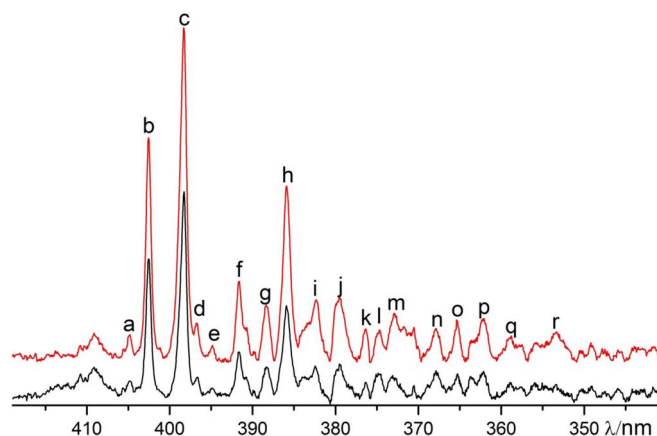
[z]E-mail: j.p.maier@unibas.ch
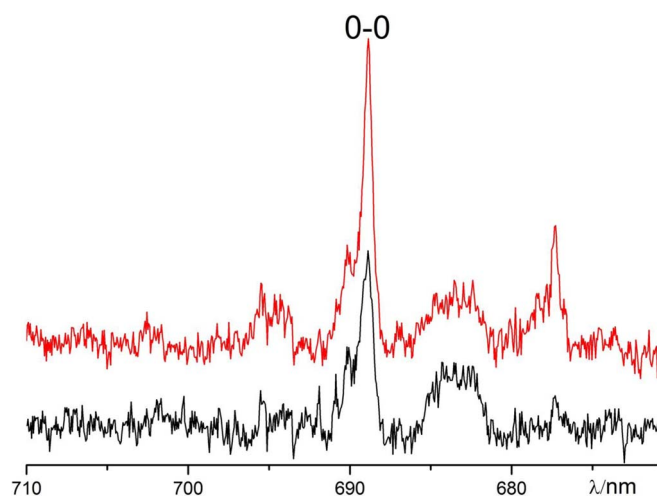
Figure 1. Electronic absorption spectrum of 1,2-dihydrogenated[60]fullerene in a 6 K neon matrix in the red of the visible region. The bottom trace was measured after codeposition of m/z = 722 in neon and the top after photobleaching with < 270 nm light.

Table I. Band maxima in the electronic absorption spectrum of the 1,2-dihydrogenated[60]fullerene, Figure 2.

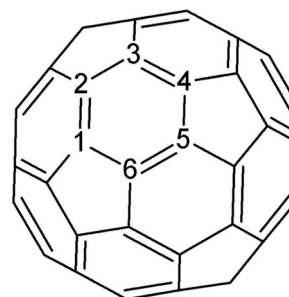| Label	λ/nm	$\tilde{v}$/cm^{-1}
a	404.8	24704
b	402.6	24839
c	398.3	25107
d	396.7	25208
e	394.8	25329
f	391.6	25536
g	388.3	25753
h	385.9	25913
i	382.3	26157
j	379.5	26350
k	376.4	26567
l	374.8	26681
m	372.9	26817
n	367.9	27181
o	365.3	27375
p	362.1	27617
q	358.9	27863
r	353.4	28297

In the electronic absorption spectrum of 1,2-dihydrogenated [60]fullerene, the first apparent band system has an origin at 404.8 nm. One of the most intense transitions is at 402.6 nm, being 20 times stronger than the 404.8 nm one. The 398.3 nm band is dominant in this region and blueshifted to this is another transition as intense as the one at 402.6 nm. These absorptions possess no site structure which is normally present in a crystalline neon matrix at 6 K.[22] It is difficult to make specific assignments of the electronic absorption spectrum of $C_{60}H_2$ because of the density of electronic states in the near-UV (Supplementary Information). Band maxima of the absorptions in the 405–350 nm region are collected in Table I.

There are three possible isomers that could be produced in the ion source: 1,2-, 1,4-, and 1,6- dihydrogenated[60]fullerenium (Figure 3). The most stable neutral has the hydrogens between two pentagons along a C=C hexagonal junction (1,2-$C_{60}H_2$). 1,4- and 1,6- $C_{60}H_2$ are 32 and 83 kJ mol^{-1}, respectively, higher in energy relative to 1,2-$C_{60}H_2$ at the B3LYP/cc-pVDZ level. This can be explained simply by the hydrogenation of unsaturated hydrocarbons. H_2 addition to a C=C bond is more favored than other pathways; this would be the most probable case for C_{60}. Additionally, theoretical investigations have

shown that 1,2-$C_{60}H_2$ is the lowest energy isomer on the potential energy surface.[23,24]

The ground-state energies of 1,2-, 1,4-, and 1,6-$C_{60}H_2$ were calculated in the C_1 symmetry group. TD-DFT was used to predict the vertical excitations at the B3LYP/cc-pVDZ level (Supplementary Information). The first dipole-allowed electronic transition for 1,2-$C_{60}H_2$ is located at 667 nm and is in good agreement with the experimental value (688.5 nm). 1,4- and 1,6-$C_{60}H_2$ have their first excited electronic state at 658 and 1058 nm; however, the oscillator strength of that for 1,4-$C_{60}H_2$ is 60 % weaker than of 1,2-$C_{60}H_2$. 1,6-$C_{60}H_2$ has a similar f -value as 1,2-$C_{60}H_2$, but these wavelengths are not within the detection range of the matrix setup.

TD-DFT predicts numerous excited electronic states for all three considered isomers in the UV. Therefore, a definite assignment for the UV absorptions would be inconclusive. There are approximately a dozen (Supplementary Information) dipole-allowed electronic transitions in the 420–350 nm region where the band system is observed (Figure 2).

1,2-$C_{60}H_2$ is not a particularly stable molecule and deprotonation of hydrogenated fullerenes can be achieved with mild bases. The high acidity of the fullerenyl C−H bond arises from the fact that $C_{60}H_2$ has pK_{a1} and pK_{a2} values of 4.7 and 16, respectively,[25] allowing for further functionalization of fullerene anions. This could be a possible mechanism known interstellar molecules to react with fullerenes. The timescales could compensate for low densities in the ISM, making the formation of substituted fullerene feasible.

Figure 2. Electronic absorption spectrum of 1,2-dihydrogenated[60]fullerene in a neon matrix at 6 K. The bottom trace was observed after deposition of m/z = 722 into neon and the top after irradiation (< 270 nm) using a medium pressure mercury lamp equipped with a water filter. Band maxima of labels a–r are given in Table I.

Figure 3. Numbering of the relevant carbon sites for C60 molecule in icosahedral symmetry.

Conclusions

A vibrationally well-resolved electronic absorption spectrum of 1,2-dihydrogenated[60]fullerene has been measured in a 6 K neon matrix. Theory and experiments show that this molecule has electronic transitions commencing at 700 nm, ca. 410 nm, and continue into the ultraviolet. This could be an encouragement for gas-phase spectroscopic studies utilizing, for example, the resonant-enhanced multiphoton ionization technique, which could then be compared directly with absorptions in the interstellar medium.[26,27] Laser ablation in the presence of methane or hydrogen molecule would be one possibility to produce $C_{60}H_2$ in a pulsed-supersonic beam, and spectroscopically, the different $C_{60}H_n$ molecules would have absorptions in specific regions of the visible spectrum.

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