

Supporting Information

Near- and Mid-IR Gas-Phase Absorption Spectra of $\text{H}_2\text{@C}_{60}^+ - \text{He}$.

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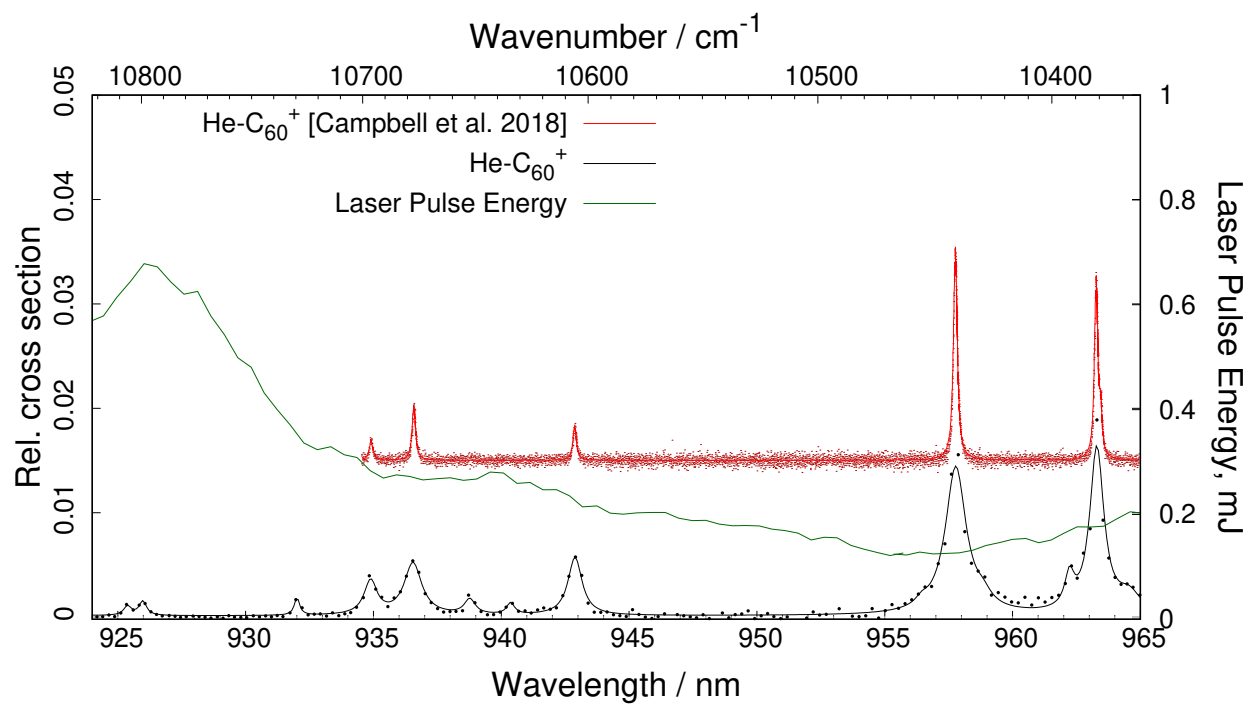


Figure S1: Comparison of our near-IR data to the Campbell and Maier¹. Here the vacuum wavelengths were converted to the air wavelengths, used in Campbell and Maier¹. The data points from Campbell and Maier¹ have been digitized using *WebPlotDigitizer*.³

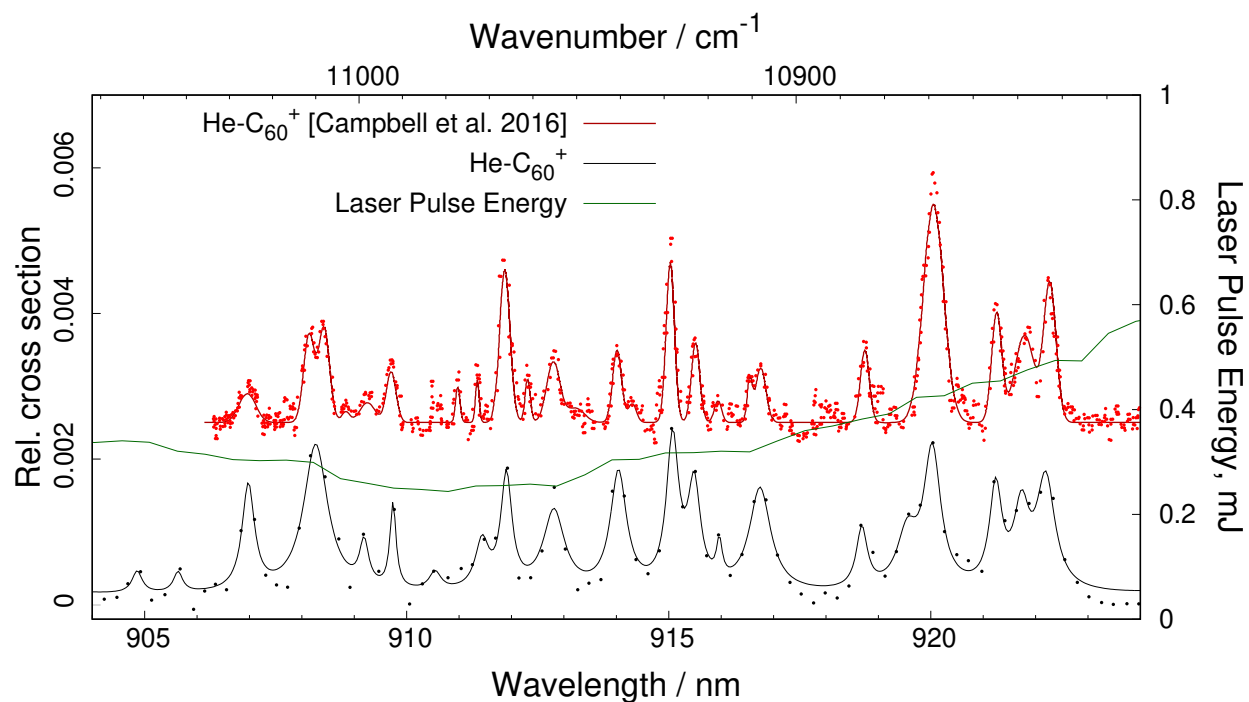


Figure S2: Comparison of our near-IR data to the Campbell et al.². Here the vacuum wavelengths were converted to the air wavelengths used in Campbell et al.². The data points from Campbell et al.² have been digitized using *WebPlotDigitizer*.³

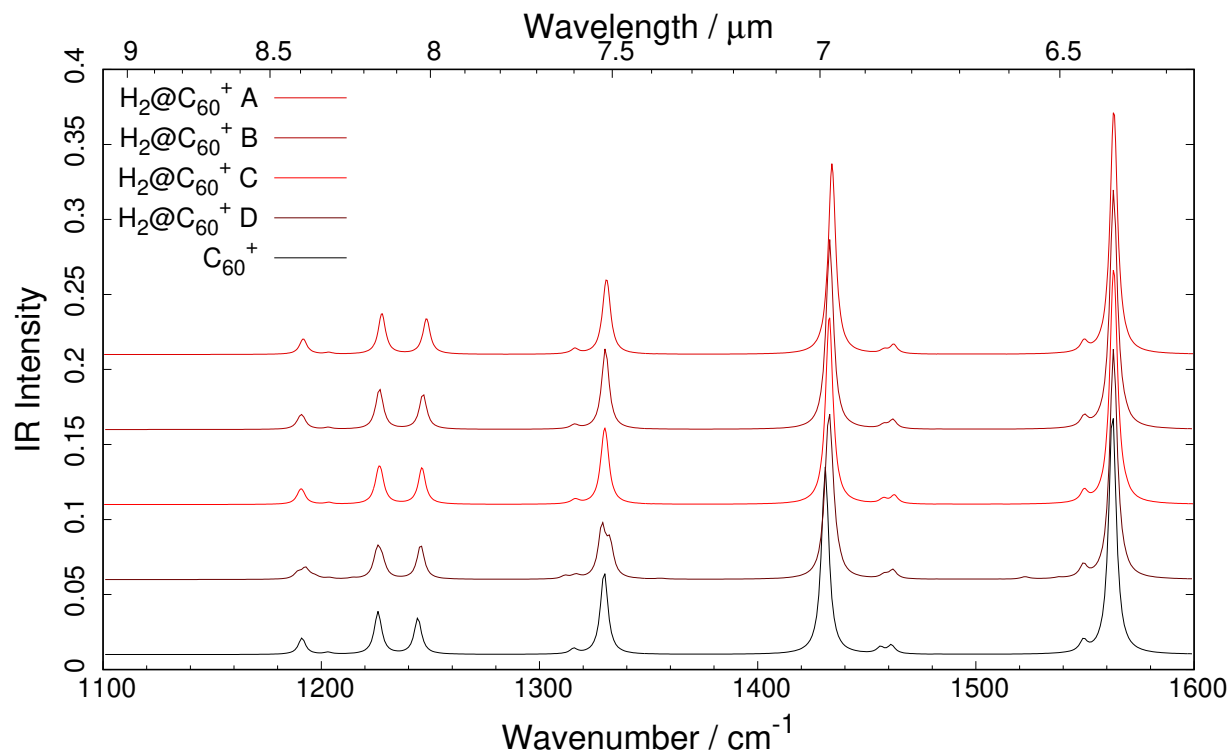


Figure S3: Calculated harmonic frequencies (RI-DFT BP86/def2-SVP, D3 dispersion correction⁴) of isomers with different H₂ orientations inside C₆₀⁺. The calculated spectrum was broadened by Lorentzian functions with a 4 cm⁻¹ FWHM. The potential energy surface for H₂ inside C₆₀⁺ is very shallow, hindering a proper geometry optimization. Therefore, we took few H₂@C₆₀⁺ isomers, which are not the real ground states due to the presence of imaginary frequencies, corresponding to H₂ motion inside C₆₀⁺. Nevertheless, the applied level of theory does not predict considerable influence of H₂ on the C-C stretching (tangential) vibrational modes.

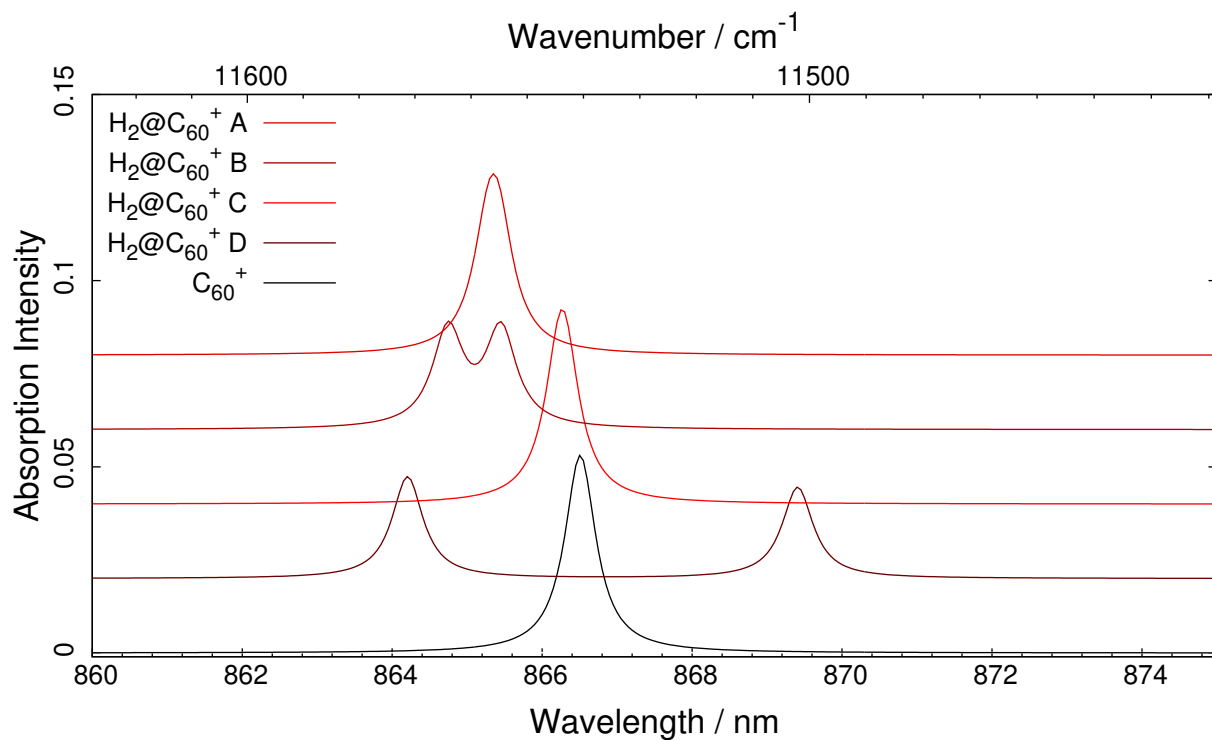


Figure S4: Calculated 0-0 vertical electronic transitions, corresponding to the $C_{60}^+ {}^2E_{1g} \leftarrow {}^2A_{1u}$ absorption (TDDFT BP86/def2-SVP)⁴ for the same $H_2@C_{60}^+$ isomers as in Fig. S3. The calculated spectrum was broadened by Lorentzian functions with a 0.5 nm FWHM: oscillator strength \times Lorentzian function. Most of the calculated absorption wavelengths show a blue shift relative to the C_{60}^+ absorption, which is also observed in the experiment.

References

- (1) Campbell, E. K.; Maier, J. P. Isomeric and Isotopic Effects on the Electronic Spectrum of C60+-He: Consequences for Astronomical Observations of C60+. *Astrophys. J.* **2018**, *858*, 36.
- (2) Campbell, E. K.; Holz, M.; Maier, J. P.; Gerlich, D.; Walker, G. A. H.; Bohlender, D. Gas Phase Absorption Spectroscopy of C₆₀⁺ and C₇₀⁺ in a Cryogenic Ion Trap: Comparison with Astronomical Measurements. *Astrophys. J.* **2016**, *822*, 17.
- (3) Rohatgi, A. WebPlotDigitizer. <https://automeris.io/WebPlotDigitizer>, Version: 4.1, E-Mail: ankitrohatgi@hotmail.com, Location: Austin, Texas, USA.
- (4) TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.