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Molecular IR Emission Spectra of Solid C_{60} and C_{70} Fullerenes

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Introduction: Cosmic abundance of fullerene molecules [1] has been a focus in astrophysics and interstellar chemistry, since the detection of the infrared (IR) emission bands of C_{60} and C_{70} in the planetary nebula [2]. A long-term mystery of DIBs has been resolved partly by the C_{60} cation in space [3]. Concerning IR absorption spectra, vibrational fingerprints of C_{60} in solid pH_2 were understood by the presence of a number of isotopomers, $^{13}C_x{}^{12}C_{60-x}$ (x = 0−3), and discussed along the Einstein's B coefficient [4]. For the estimation of molecular abundance in space, vibrational temperature is crucial, because the IR emission requires population of molecules in their vibrationally excited states.

[1] Kroto, H.W.; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. C_{60}: Buckminsterfullerene. *Nature 318*, 162, **1985**.
[2] Cami, J.; Bernard-Salas, J.; Peebles, E.; Malek, S.E. Detection of C_{60} and C_{70} in a young planetary nebula. *Science 329*, 1180, **2010**.
[3] Campbell, E.K.; Holz, M.; Gerlich, D.; Maier., J.P. Laboratory confirmation of C_{60}^+ as the carrier of two diffuse interstellar bands. *Nature 523*, 322-323, **2015**.
[4] Wakabayashi, T.; Momose, T.; Fajardo, M.E. Matrix isolation spectroscopy and spectral simulations of isotopically substituted C_{60} molecules. *J. Chem. Phys. 151*, 234301, **2019**.

C_{60} and C_{70} in Space

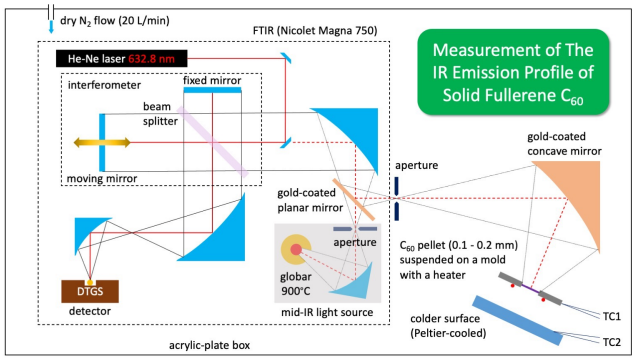
- ✓ Anticipated since the discovery in **1985** by Kroto, Curl, and Smalley.
- ✓ Discovered in planetary nebulae in **2010** by Cami and co-workers.
- ✓ Identified as the C_{60} cation for the NIR diffuse interstellar bands (DIBs) in **2015** by Campbell, Gerlich, and Maier.

➢Abundance of fullerenes in space still remains a challenge!

➢Physical properties of the IR emission are crucial.

➢IR emission spectra are measured in the laboratory (This work).

FTIR Spectrometer (N_2-purged)



Sample

a) Thin films of C_{60} deposited on a KBr slab (2-3 microns)
b) Pressed pellets of C_{60} and C_{70} (~0.2 mm, free standing)

Heater: ~7.2 W (up to 110°C)

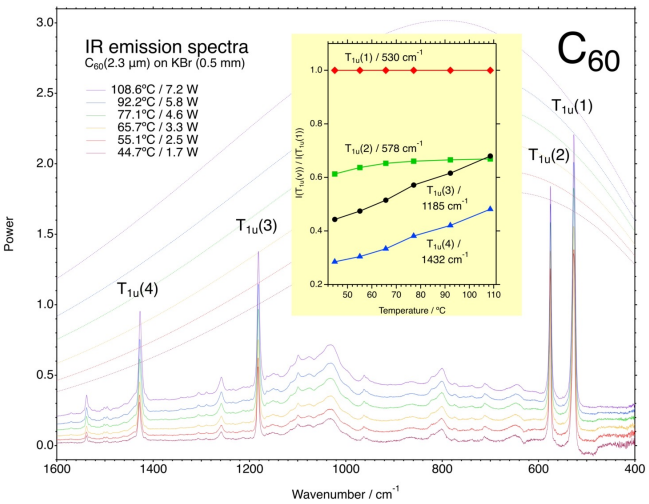
Measurements

FTIR: Nicolet Magna 750

- Resolution >0.5 cm^{-1}
- Acquisition 4096

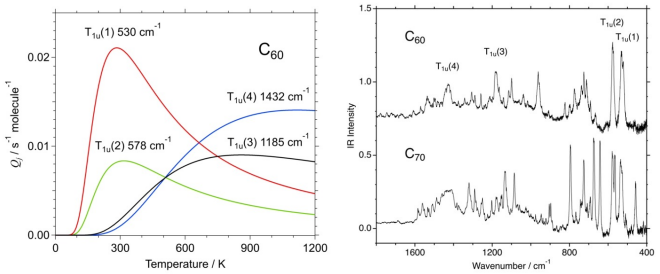
Thermal emission of the C_{60} sample was detected to obtain its power spectrum for an external light source, instead of a spectrum of the mid-IR light source, a globar at ~900°C.

IR Emission of a Thin Film of C_{60}/KBr@45−110°C



- ➢ Emission bands of the four IR-active vibrational modes of I_h-C_{60} are intensified as the temperature is increased.
- ➢ The intensification is higher for the higher-frequency modes (inset).

Theoretical Simulations & IR Emission of C_{60}/C_{70} Pellets@80 °C



- ➢ Temperature dependence of the relative intensity among the four T_{1u} modes the is simulated theoretically (left).
- ➢ For solid C_{60} and C_{70} pellets at 353 K (80°C), emission bands of the IR-active vibrational modes are saturating to the blackbody contour and those of **combinations** and **overtones** are intensified concomitantly (right); cf., Wang, K.-A.; Rao, A.M.; Eklund, P.C.; Dresselhaus, M.S.; Dresselhaus, G. Observation of higher-order infrared modes in solid C_{60} films. *Phys. Rev. B 48*, 11375, **1993**.

Conclusions & Noteces

➢**In this work**, molecular IR emission bands of solid C_{60} and C_{70} fullerenes were observed at elevated temperature of 45−110°C. Analyses of the temperature dependence of relative intensities of the IR-emission bands are in progress. This work has been supported by JSPS KAKENHI 20K05438. "*Infrared emission mechanism of fullerene C_{60} and its cosmic abundance*"

➢**Notice: The COST Action** CA21126 has been approved and will start in September 2022; "*Carbon molecular nanostructures in space.*" Young researchers from EU countries are participating.