The infrared emission spectrum of gas-phase C_{60} (buckminsterfullerene)

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The gas-phase infrared spectrum of C_{60} has been observed in emission with the National Solar Observatory Fourier transform spectrometer at Kitt Peak. Bands attributable to the C_{60} molecule are found at 527.1, 570.3, 1169.1 and 1406.9 cm^{-1}. Additional emission features are tentatively assigned to C_{70} or combination bands of C_{60}. A new, strong emission is observed at 1010.2 cm^{-1} belonging to an unknown molecule. None of these features can be associated with any of the strong emission bands observed so far in astronomical sources.

Since the original report on the existence of buckminsterfullerene (C_{60}) [1] there has been considerable interest in the spectroscopy of it and related all-carbon molecules. Such molecules may be abundant in astronomical environments and may have desirable practical applications as, for example, coatings and catalysts. Until the recent development of a simple method to prepare gram quantities of reasonably pure C_{60} [2] there were only two experimental reports of C_{60} optical spectra [3,4]. Electronic spectra in the ultraviolet have been obtained by several groups [2-5] and a theoretical prediction is available [6]. Photoelectron spectra have also been obtained [7-9]. Vibrational Raman spectra of purified films of C_{60} and C_{70} were recently measured [10]. Infrared vibrational spectra have been reported from solid films [2,4], pressed KBr pellets [11], and in an argon matrix [11], but all at low resolution. A number of theoretical calculations of the infrared spectrum of C_{60} have been made [12-17]. However, gas-phase spectra of the free C_{60} molecule are more useful for comparison with astronomical spectra. Closely related calculations on the spectra of atoms trapped within a C_{60} cage have also been made

with the possibility of explaining the diffuse interstellar lines [18,19].

The gas-phase infrared spectrum of C_{60} in the ground electronic state was recorded with the National Solar Observatory Fourier transform spectrometer (FTS) associated with the McMath solar telescope at Kitt Peak. The unapodized resolution was 0.005 cm^{-1} with liquid-helium-cooled As:Si detectors and a KCl beam splitter. The spectral bandpass was limited to 500–1400 cm^{-1} with an InSb filter or 500–2800 cm^{-1} with an InAs filter. Infrared radiation from a SiC glower was passed through the absorption cell and focused on the 8 mm entrance aperture of the FTS. The entire path between glower and entrance aperture was purged with dry nitrogen, and the FTS was operated in vacuum. For the emission spectra, the glower was simply switched off. For most spectra, three scans were co-added for 15 min of integration.

Approximately one gram of crystalline C_{60} was produced using the technique described earlier by Krätschmer et al. [2]. It was expected that C_{70} fullerene would be the main impurity, but no analysis was made prior to our experiment. Later, however, we learned that our sample contained considerable

amounts of C_{70} (10–15%) as measured using size exclusion chromatography.

Initially, we recorded the infrared absorption spectrum of solid C_{60} deposited as a thin film onto a silicon substrate by vacuum sublimation. The brownish film was estimated to be a few microns thick. The measured peak absorptions agree very well with the values reported previously [2]. Table 1 lists the bands attributable to the solid C_{60} film. As anticipated, no structure in this condensed-phase spectrum was observed.

Gas-phase C_{60} was produced in an alumina tube furnace described earlier in a study of infrared emission spectrum of SiS [20]. The furnace consisted of an alumina tube (0.9 m long and 50 mm diameter) to which a gas inlet, a pumping port and KBr windows were attached with "O-ring"-sealed fittings. About 1 g of the C_{60}/C_{70} mixture was placed in the middle of a quartz tube (0.8 m long and 36 mm outer diameter, 32 mm inner diameter) which was used as a liner in the alumina tube. The furnace was slowly heated to 200°C with a slow flow of argon at 2 Torr to drive off water and hydrocarbons. The system was then pressurized with pure argon at 5 Torr and sealed.

A series of spectra was taken as the furnace temperature was raised at a rate of about 2°C/min. The pressure in the cell gradually increased to 11 Torr as the temperature reached 500°C, when a rapid change in pressure to about 15 Torr was observed. New absorption features appeared and their intensities increased as the temperature was raised. No absorption features corresponding to the solid C_{60} spectrum were observed. The positions of the four broad absorption bands are 817.4, 1034.0, 1091.1 and 1264.1 cm^{-1}. At high resolution these bands did not show

structure, indicating the presence of a large absorbing molecule perhaps a "plastic" material formed at the same time as C_{60} from graphite. At about 750°C, the glower was switched off and infrared emission from the cell was observed. Several emission spectra were recorded as the cell was heated to a maximum temperature of about 950°C. At this temperature, the intensity of the C_{60} emission features started to decrease dramatically, and did not reintensify as the furnace was cooled.

After cooling the furnace to near ambient temperatures and removing the quartz tube, it was found that the toluene-soluble crystalline material was deposited in rings near the ends of the tube, corresponding to the lower temperature zones of the furnace. In the center, were the original C_{60} sample was placed, a substantial pile of a black powder was found. This proved to be toluene-insoluble and an X-ray powder analysis indicated that this powder was amorphous carbon. This suggests that C_{60} may revert to a soot-like carbon near 950°C. Note that small amounts of air leaked into the cell which could also contribute to the transformation of the initial material. The presence of impurities is confirmed by strong emission features due to CO_2 and CH_4. This observed transformation may be of significance if C_{60} emission or absorption can be observed in astronomical sources, since this would set an upper limit to the local temperature.

The emission spectrum of C_{60}/C_{70} mixture is shown in figs. 1a and 1b. The IR bands attributed to C_{60} are shown with the horizontal scale expanded by a factor of 6 in fig. 2. The band frequencies and their full-width at half maximum (fwhm) are reported in table 1. Also a comparison with the solid-state spec-

Table 1
The infrared vibrational frequencies of C_{60} (in cm^{-1})

Mode	Gas phase this work	Solid state		Argon matrix ref. [11]
		this work	ref. [2]	
1	527.1 (11) [a]	527.0	528	530.1 (1) [a]
2	570.3 (13) [b]	576.6	577	579.3 (2)
3	1169.1 (13)	1182.7	1183	1184.8 (2)
4	1406.9 (12)	–	1429	1431.9 (4)

[a] The full-width at half maximum is reported in parentheses.
[b] This band shows some structure (fig. 2) reminiscent of a P (563.1 cm^{-1}), Q (570.3 cm^{-1}) and R (575.3 cm^{-1}) contour.
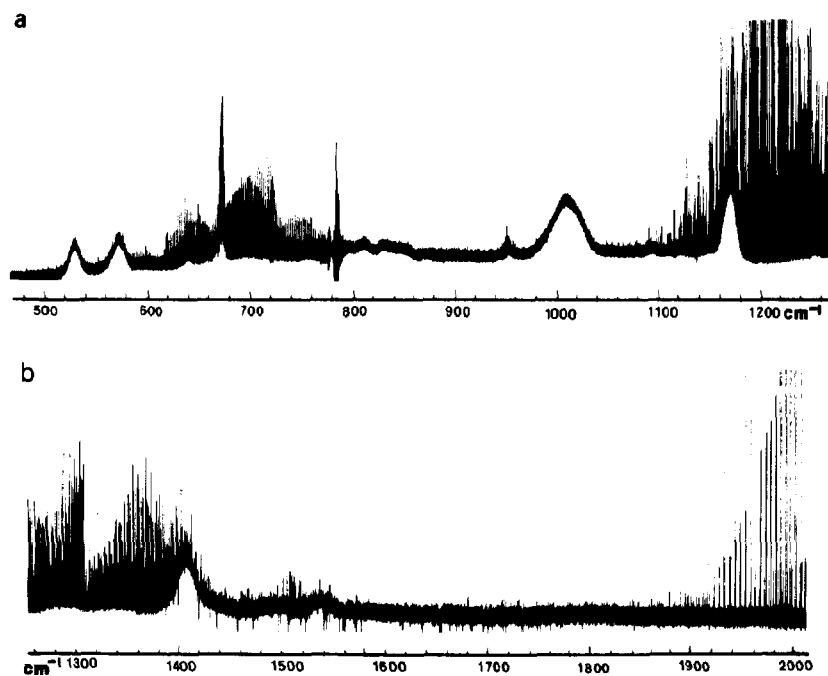
Fig. 1. Low dispersion emission spectra of C_{60}/C_{70} mixture. (a) The 500–1300 cm^{-1} region limited by an InSb filter. (b) The 1250–2000 cm^{-1} region using an InAs filter. Note the presence in the spectra of other emission features.

trum is shown in this table. Small blue shifts of about 20 cm^{-1} are not inconsistent with matrix shifts for other molecules.

There is little evidence of rotational structure. The only C_{60} feature which shows a structure reminiscent of P, Q, and R branches is the band at 570.3 cm^{-1}. This vibrational band has a maximum at 570.3 cm^{-1} and lower intensity shoulders at 563.1 and 575.3 cm^{-1}. However, this structure could be due to the overlap of other unknown infrared bands. The solid phase spectrum of this band is also asymmetric.

Besides the very small rotational constant (β = 0.0028 cm^{-1}), several factors can contribute to the complexity of the spectrum. At high temperatures, not only are hot bands quite likely to be important, but rotational quantum numbers approaching 1000 are predicted. While this discussion has assumed that the species responsible is C_{60}, the presence of C_{70} may also contribute overlapping bands. In addition, C_{60} is primarily composed of $^{12}C_{60}$ (51%) and $^{12}C_{59}{}^{13}C$ (34%) isotopomers, assuming that ^{13}C has a natural abundance of 1.1%. The $^{12}C_{59}{}^{13}C$ isotopomer has much lower symmetry (C_s) than $^{12}C_{60}$, in addition

to being a slightly asymmetric top, and thus more complex spectral structures might be expected.

The peak positions of the infrared bands of C_{60} reported in table 1 will differ slightly from the actual gas-phase band origins. Because of vibrational anharmonicity the hot bands will contribute more intensity to the red side of the band origins for the hot C_{60} band contours. The extents of the red shifts are difficult to calculate since the vibrational anharmonicities are unknown. Experimentally the position of the band at 1169.1 cm^{-1} shifts by about 2 cm^{-1} when the temperature is changed by 200°C. This suggests that the actual band origin may be as much as 10 cm^{-1} to the blue, close to the Ar matrix value of 1184.8 cm^{-1}.

Surprisingly, the widths of the infrared bands are changed very little by the presence of hot bands. Weeks and Harter [17] calculate that the four strong bands of C_{60} will have full-widths at half maximum of 5.5, 7.5, 6.7, and 10.7 cm^{-1} at 293 K not including hot band contributions. At our temperature of 1065 K the expected band widths are 10.5, 14.3, 12.8, and 10.3 cm^{-1} compared to the observed widths of
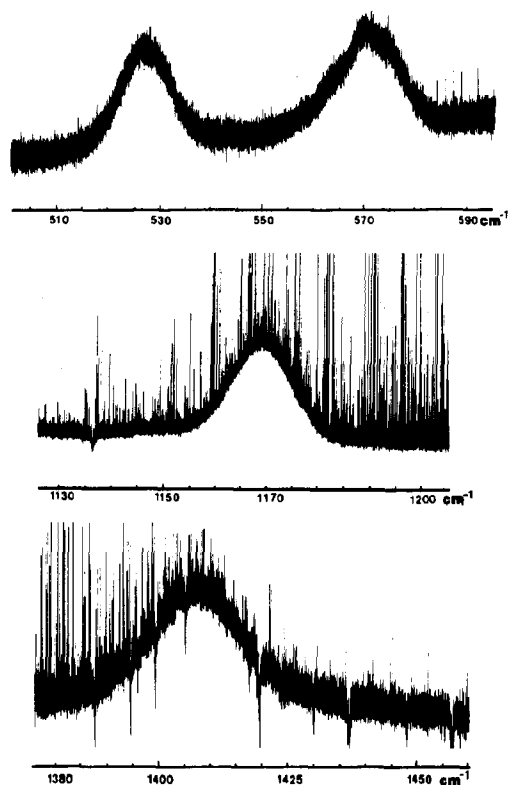
Fig. 2. The infrared emission bands attributed to C_{60}. The horizontal scale was expanded by a factor of six relative to fig. 1. Note the structure associated with the band at 570.0 cm^{-1}.

11, 13, 13, and 12 cm^{-1} for modes 1–4 respectively, assuming that the band widths scale as the square root of the ratio of the temperatures. The presence of 174 slightly anharmonic modes in C_{60} drains the population from the ground vibrational level which shifts the band positions but leaves the widths of the contours unchanged. In fact the shift and width of the bands can be used as a thermometer for laboratory and astronomical sources.

Numerous additional weak emission features, for example, at 638.3, 670.9, 951.3 and 1539.3 cm^{-1}, probably attributable to C_{70} or some IR allowed combination bands of C_{60} are also found. While impurities cannot be ruled out, these features are also present in the solid-state spectrum of Krätschmer et al. [2]. As expected, these frequencies are shifted to the red in the gas phase spectrum. A strong emission band of unknown identity appeared around 1010.2 cm^{-1} (with a fwhm of 32 cm^{-1}) at elevated tem-

peratures. The intensity of this band decreased as the furnace temperature approached the maximum and completely disappeared as the cell cooled down.

Finally, none of these gas phase infrared bands correspond to any of the strong emission bands observed so far in astronomical sources. However, we believe that our measurements will facilitate the search for C_{60} in space.

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