

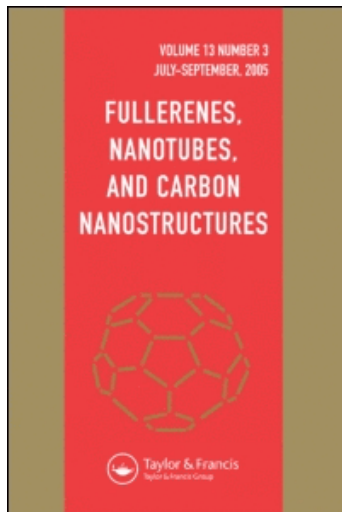
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Low and High Temperature Infrared Spectroscopy of C₆₀ and C₇₀ Fullerenes

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The FT-IR spectra of the fullerenes C₆₀ and C₇₀ have been recorded in the temperature range between 523 K (+250°C) and 93 K (–180°C). As a general rule, it has been observed a shift of the infrared absorption bands toward higher frequencies at lower temperatures. As expected, at 93 K the infrared spectra appear better resolved with sharper absorption bands and higher intensity than the same bands measured at higher temperature. All the infrared spectra of the present study have been made on samples embedded in KBr matrix and all data were extrapolated to 0 K. These spectral data at extremely low temperatures are of paramount importance for astrochemical search of these molecules in space. By comparing the gas phase spectra of both C₆₀ and C₇₀ fullerenes extrapolated to 0 K with the data taken in KBr matrix, the gas phase spectral bands were found systematically shifted 5–10 cm^{–1} toward higher frequencies than the same bands recorded in KBr. Similarly, the matrix effect is appreciable also when the spectral data taken in KBr are extrapolated to >1000 K. In such case the band position of C₆₀ and C₇₀ fullerenes in the gas phase are shifted to lower frequencies than the extrapolation data taken in KBr matrix.

Keywords Astrochemistry, band shift, C₆₀, C₇₀, FT-IR spectroscopy, fullerenes, gas phase spectra, low temperature spectra

Introduction

The vibrational spectroscopy of C₆₀ and C₇₀ fullerenes has been investigated in numerous papers and reviewed by Kuzmany and colleagues (1,2). Much less attention has been devoted to the low temperature and extremely high temperature spectra of these two molecules. From the astrochemistry point of view, it is extremely important to know the low temperature spectra of molecules which can be the object of research in the space. Similarly, also the high temperature gas phase spectra are of high importance in the search of molecules in an extremely warm environment. In particular fullerenes are thought to be present in the circumstellar environment of late-type carbon-rich stars probably mixed or embedded with other forms of elemental carbon (3). Particularly remarkable sources of fullerenes are thought to be the *R Coronae Borealis* (*RCorBor*) class of stars because must present the best environmental conditions for fullerene formation, being carbon giant stars helium-rich and depleted in hydrogen (4). These stars are pulsating like the Cepheids but irregularly. Thus, it may happen that their magnitude drops suddenly, recovering sometimes

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quickly, other times taking months. The dimming comes from irregular clouds of carbon dust ejected by the stars, perhaps as a result of pulsation (5). The research of fullerenes in the *RCorBor* stars until now has produced contradictory and uncertain results (6,7). Instead, C_{60} fullerenes have been recently detected with the Spitzer/IRS telescope in the infrared spectra of the reflection nebulae NGC 2023 and NGC 7023 (8).

The present work is dedicated to the analysis of the low temperature infrared spectra of C_{60} and C_{70} fullerenes, the extrapolation of the absorption bands to 0 K as well as the extrapolation of the spectral data taken in the range of 93 K to 523 K to ≈ 1100 K. The spectral data extrapolated to 1100 K were compared with experimental gas phase data taken at the same temperature.

Experimental

Materials and Equipment

C_{60} and C_{70} fullerenes were 99% pure chemicals from MTR Ltd (USA). Infrared spectrophotometric grade KBr was obtained from Aldrich (USA).

The FT-IR spectra were recorded on samples embedded in KBr pellets at a resolution of 4 or 1 cm^{-1} on a spectrometer Nicolet IR-300 from Thermo-Fischer Corp. (USA).

The low temperature apparatus attached to the spectrometer consisted of a variable temperature cell from Specac model P/N 21525 equipped with KBr windows and sample holder which is able to work in the range between 523 K and 93 K.

Experimental Procedure

A fullerene sample (C_{60} or C_{70}) embedded in KBr was mounted into the sample holder of the Specac variable temperature cell and inserted into the cell. The cell was then evacuated with the aid of a pump to a vacuum of 0.1 torr and heated or cooled to the desired temperature. Heating was provided by an external temperature control system using the Joule effect; for cooling below room temperature, use was made of liquid nitrogen added into the cavity present inside the cell. The temperature of the sample was monitored with adequate thermocouples. The lowest temperature reached with this apparatus was 93 K and the highest temperature was 523 K. All the spectral processing operations, change of scale from cm^{-1} to μm were made through the Omnic software of our infrared spectrometer.

Results and Discussion

Low Temperature and High Temperature Gas Phase FT-IR Spectra of C_{60} Fullerene

Fullerene C_{60} has the highest symmetry of any known molecule. Although there are 174 vibrational degrees of freedom ($3N-6$) for each C_{60} molecule, the icosahedral symmetry of the fullerene C_{60} gives rise to a number of degenerate modes, so that only 46 mode frequencies are expected for this molecule. Of these, four are infrared-active and 10 are Raman-active, whereas the remaining modes are optically inactive (1,2).

The infrared spectrum of C_{60} is very simple, consisting of four modes with F_{1u} symmetry observed at frequencies of 527 ($F_{1u}(1)$), 576 ($F_{1u}(2)$), 1182 ($F_{1u}(3)$) and 1429 ($F_{1u}(4)$) cm^{-1} . The 527 and 576 cm^{-1} modes are associated with a primarily radial motion of the carbon atoms, while the 1182 and 1429 cm^{-1} modes are essentially associated with a tangential motion of the carbon atoms (1,2). The most characteristic vibrational mode is the pentagonal

“pinch” mode at 1429 cm^{-1} . When C_{60} is cooled to 260 K, a phase transition occurs to a state with a high degree of orientational order referred to as the “ratchet phase” (9). On further cooling the C_{60} crystals between 150 K and 90 K, a glass transition can be observed because C_{60} molecules shuffle into two nearly degenerate orientations. On further decreasing temperatures, the population of C_{60} molecules with energetically less favorable orientation decrease but do not vanish completely. Even below 90 K, about 17% of the C_{60} is found to be frozen in the energetically less favorable orientation, leading to a glass-like behavior (1,2,9). Such transitions can be followed by plotting the relative intensity or the peak height of the 4 infrared absorption bands as a function of the temperature (9,10).

The FT-IR spectra of C_{60} measured with our apparatus at 523 K, 348 K and 93 K are reported in Figure 1. The well-known phenomena of band sharpening and increase in their intensity can be easily observed. In other words, at low temperature the infrared spectrum results better resolved. Such phenomenon can be better appreciated in Figure 2 where the synthetic spectrum derived from the subtraction of the low temperature (93 K) spectrum of C_{60} from that recorded at 523 K is reported. The peaks pointing downward are due to the low temperature spectrum: $6.988\text{ }\mu\text{m}$ (1431 cm^{-1}), $8.443\text{ }\mu\text{m}$ (1184 cm^{-1}), $17.316\text{ }\mu\text{m}$ (577 cm^{-1}), $19.044\text{ }\mu\text{m}$ (525 cm^{-1}). The peaks pointing upward are due to the high temperature spectrum: $6.946\text{ }\mu\text{m}$ (1440 cm^{-1}) and $7.052\text{ }\mu\text{m}$ (1418 cm^{-1}), $8.422\text{ }\mu\text{m}$ (1187 cm^{-1}) and $8.506\text{ }\mu\text{m}$ (1176 cm^{-1}), $17.210\text{ }\mu\text{m}$ (581 cm^{-1}) and $17.484\text{ }\mu\text{m}$ (560 cm^{-1}), $18.833\text{ }\mu\text{m}$ (531 cm^{-1}) and $19.191\text{ }\mu\text{m}$ (521 cm^{-1}). It is evident from the spectrum in Figure 2 that the bandwidth was larger at higher temperature and became narrower at low temperature. This behavior of the C_{60} infrared

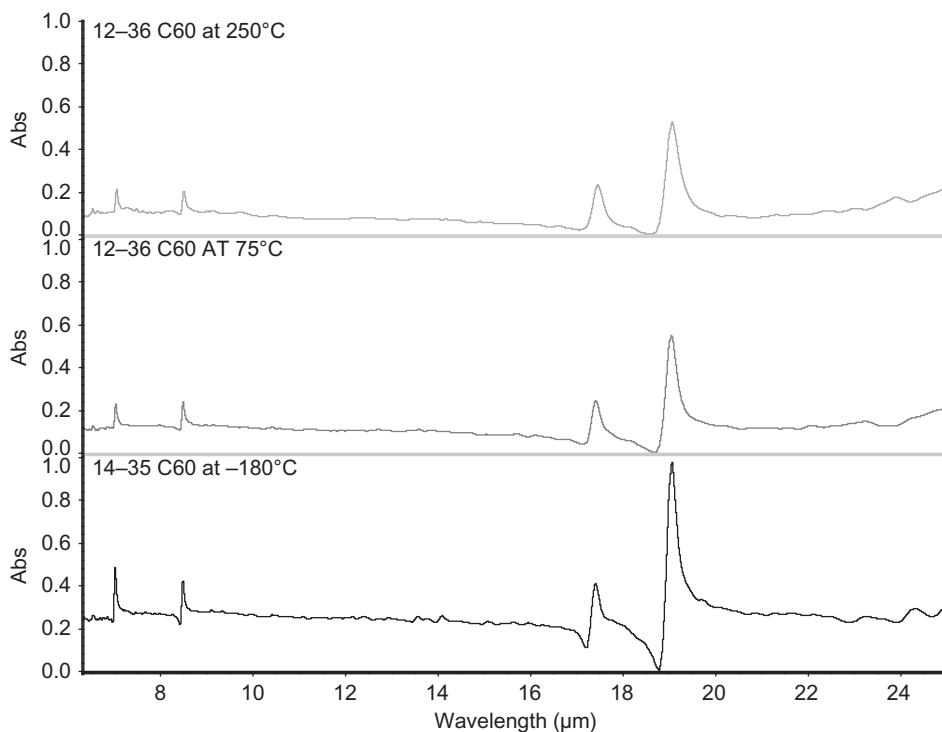


Figure 1. FT-IR spectra of C_{60} in KBr taken respectively (from top to bottom) at 523 K ($+250^{\circ}\text{C}$), 348 K ($+75^{\circ}\text{C}$) and at 93 K (-180°C).

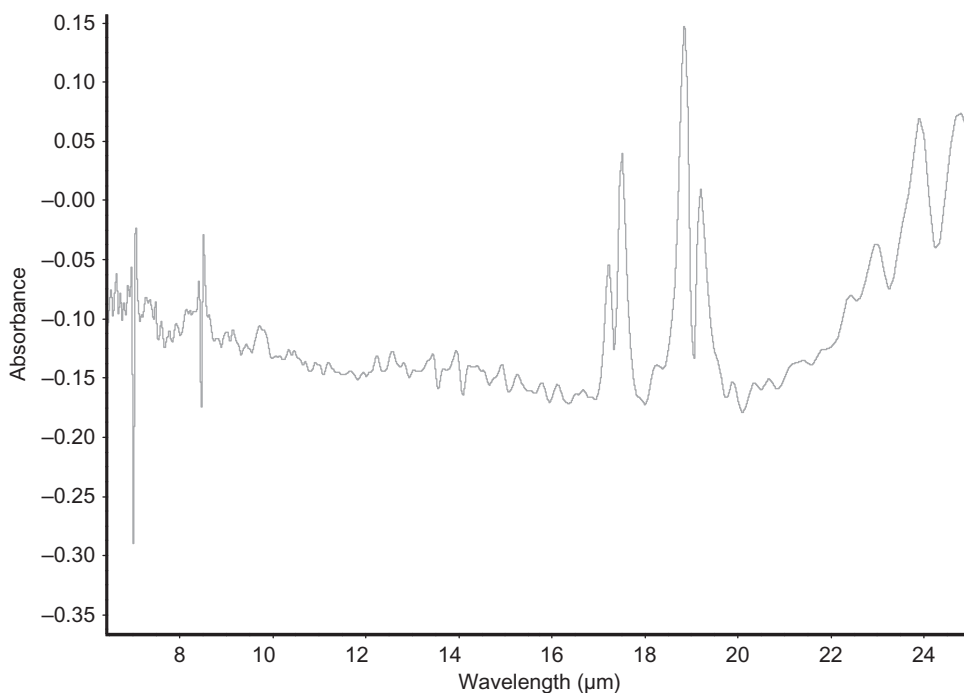


Figure 2. Spectrum derived from the subtraction of the low temperature 93 K (-180°C) spectrum of C_{60} from that recorded at 523 K ($+250^\circ\text{C}$). The peaks pointing downward are due to the low temperature spectrum: 6.988 μm , 8.443 μm , 17.316 μm , 19.044 μm . The peaks pointing upward are due to the high temperature spectrum: 6.946 and 7.052 μm , 8.422 and 8.506 μm , 17.210 and 17.484 μm , 18.833 and 19.191 μm . It is evident from such spectrum the bandwidth was larger at higher temperature and became narrower at low temperature.

absorption spectrum toward temperature was already reported and analyzed by Frum et al. (11) and Nemes et al. (12).

An additional feature of the low temperature spectra of C_{60} is the shift of the infrared band position. Such phenomenon is illustrated in Figure 3 on the $F_{1u}(3)$ band of C_{60} . On lowering the temperature from 523 K to 93 K, the absorption peak originally located at 1178 cm^{-1} shifts to higher frequencies i.e. 1182 cm^{-1} . In addition, the bandwidth is reduced from 8.95 cm^{-1} to 7.97 cm^{-1} respectively from 523 K to 93 K and the peak area passes from 2.275 to 2.400 since at lower temperature there is a sharpening of the absorption band but also an increase in intensity. It is known that even in the solid state the C_{60} molecules rotate at high temperature and there is an interaction between adjacent molecules; the coupling of the vibration with the diffuse rotation is the cause of the band broadening effect. On cooling the rotation is inhibited, and also there is a decay of the vibration into a lower lying optical mode and a lattice mode (2).

By measuring the infrared peak position of C_{60} at different temperatures in the range of 523 K to 93 K, it is possible to know by extrapolation the peak position at 0 K, an important information for the search of the fullerene infrared "signature" in the interstellar or circumstellar medium. Figure 4 illustrates the procedure for the pentagonal "pinch" vibrational mode of C_{60} : the peak position at three different temperatures are plotted against the temperature and the resulting linear dependence of peak position with temperature is employed to determine the infrared absorption peak position of C_{60} at 0 K. As shown in Figure 4, the expected peak position of the pentagonal "pinch" vibrational mode of C_{60} at

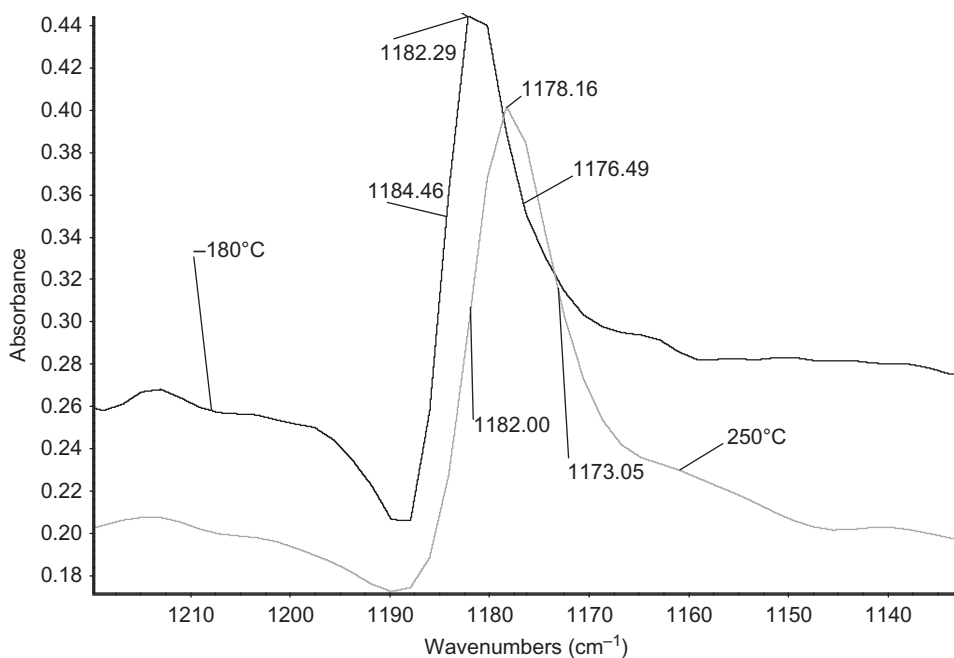


Figure 3. FT-IR spectra of C_{60} (in KBr). On lowering the temperature from 523 K (+250°C) to 93 K (−180°C) the absorption peak originally located at 1178 cm^{-1} shifts at higher frequencies, that is, 1182 cm^{-1} . Additionally, the bandwidth is reduced from 8.95 cm^{-1} to 7.97 cm^{-1} , respectively, from 523 K (+250°C) to 93 K (−180°C), and the peak area passes from 2.275 to 2.400 since at lower temperature there is a sharpening of the absorption band but also an increase in intensity.

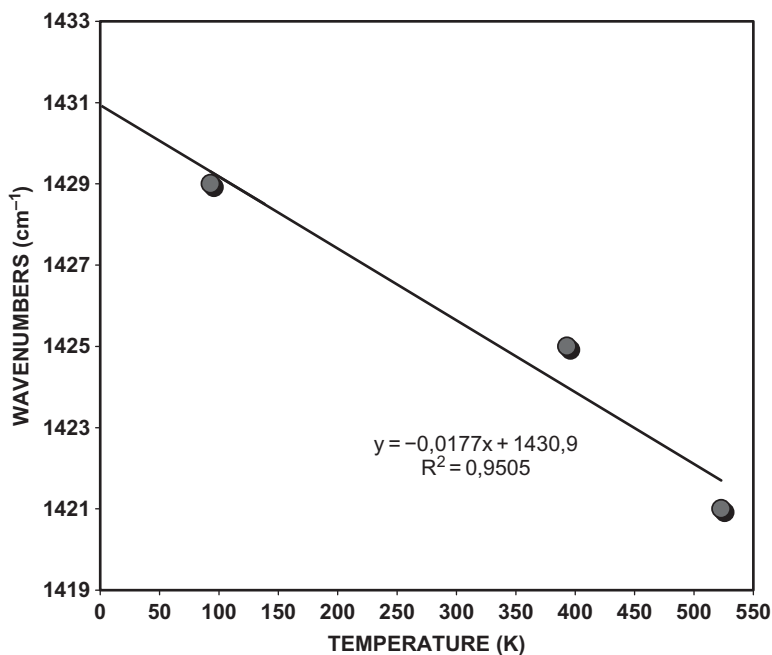


Figure 4. Extrapolation to 0 K of the C_{60} infrared absorption band position. This is the case of the $F_{1u}(4)$ band, the pentagonal “pinch” mode. The intercept at 0 K occurs at 1430,9 cm^{-1} .

0 K is 1430.9 cm^{-1} , about 9.7 cm^{-1} higher frequency than the band position at 523 K. In Table 1 the peak position of all 4 absorption bands of C_{60} extrapolated to 0 K are reported. As already reported previously, our infrared measurements on C_{60} were made in a KBr matrix. The vibrational frequencies of the gas phase spectra of C_{60} taken in the range of temperature comprised between 879 and 1212 K were extrapolated to 0 K to give the theoretical position of these bands: an approach of astrochemical interest (12). The results of that extrapolation are reported in Table 1. It can be observed that the vibrational frequencies at 0 K derived from the gas phase data are shifted toward higher wave numbers in comparison to the data derived from C_{60} in KBr matrix (and extrapolated to 0 K) by 6.2 cm^{-1} for the $F_{1u}(1)$ mode, by 7.7 cm^{-1} for the $F_{1u}(3)$ and by 4.6 cm^{-1} for the $F_{1u}(4)$ mode. Instead only the $F_{1u}(2)$ mode the band extrapolated to 0 K is shifted to shorter wave numbers by 2.4 cm^{-1} in comparison to the data in KBr matrix extrapolated at 0 K.

In Table 1 are reported the positions of the infrared peaks of C_{60} in other environments. It is interesting to compare the infrared data taken at 83 K in an Ar matrix with our data recorded at 93 K in KBr matrix. The four infrared band frequencies of C_{60} are shifted toward higher wave numbers from 2.5 to 6.1 cm^{-1} for the C_{60} sample embedded in Ar matrix suggesting lower interaction with matrix in comparison to the sample imbedded in KBr matrix but also lower degree of freedom of the molecules and perhaps a much more C_{60} - C_{60} -lattice interaction. Furthermore, also the values of full-width at half maximum (fwhm) of the absorption bands reported in parenthesis in Table 1 show significant differences, being significantly smaller for the C_{60} sample in Ar matrix, in line with the explanation already given for the frequency shift.

Frum et al. (11) as well as Nemes et al. (12) have studied the gas phase spectra of C_{60} above 1000 K. Their data are reported in Table 1. At the mentioned temperatures it is not surprising to find fwhm values above 10 cm^{-1} attributable to the high rotational freedom of the molecules at these temperatures. It is interesting to note that fwhm of the same order of magnitude were found in our infrared study on C_{60} in a KBr matrix and heated at 523 K. By extrapolating the vibrational frequencies measured at 523 K in KBr to 1083 K using the following equations:

$$\nu_{F_{1u}(4)} = -0.0177T + 1430.9$$

$$\nu_{F_{1u}(3)} = -0.00884T + 1183.0$$

$$\nu_{F_{1u}(2)} = -0.0063T + 576.8$$

The expected infrared frequencies at 1083 K in KBr are: 570.0, 1173.4 and 1411.7 cm^{-1} . By comparing these values with the gas phase values reported in Table 1, it can be observed that at high temperature the matrix effect of KBr affects only the bands at 1173.5 and 1412.0 cm^{-1} causing a shift to higher frequencies respectively of 4.5 and 7.6 cm^{-1} in comparison to the gas phase bands. The band at 570 cm^{-1} appears independent from temperature.

A simplified model which can be used to explain the low temperature infrared band shift is offered by the harmonic oscillator of two masses connected by a spring (a model of two atoms linked by a chemical bond):

$$\nu_n = (2\pi c)^{-1}(k/\mu)^{1/2} = (2\pi c)^{-1}(F/x\mu)^{1/2}$$

where ν_n is the vibrational frequency in wavenumber, c the velocity of light, k the force constant and μ the reduced mass of the system. Applying the Hooke's law, the force constant $k = F/x$ with F the force acting on the two masses and x their displacement. By lowering the temperature of the system the displacement of the masses is minimized, the force constant

Table 1
Summary of C₆₀ infrared absorption bands and width (fwhm in parenthesis) in cm⁻¹

0 K (*)	0 K (**)	83 K (**)	93 K (*)	523 K (*)	1065 K (**)	1083 K (***)	1083 K	1083 K
KBr matrix	gas phase	Ar matrix	KBr matrix	KBr matrix	gas phase	gas phase	KBr matrix	gas/KBr
extrap. to 0 K	extrap. to 0 K						extrap. to 1083 K	difference
1430.9	1435.5	1431.9 (4)	1428.9 (10.8)	1421.2 (10.7)	1406.9 (12)	1407.2 (13.5)	1411.7	-4.5
1183.0	1190.7	1184.8 (2)	1182.3 (7.9)	1178.2 (8.9)	1169.1 (13)	1165.8 (n.d.)	1173.4	-7.6
576.8	574.4	579.3 (2)	574.7 (6.9)	572.7 (10.0)	570.3 (13)	570.0 (13.7)	570.0	0.0
525.0	531.2	530.1 (1)	524.0 (6.9)	524.0 (8.8)	527.1 (11)	527.5 (11.6)		

(*) This work.

(**) From ref. (11).

(***) From ref. (12).

increased and thus the vibrational frequency is increased. It can be calculated for the C-H band that an increase of the force constant of 0.2% leads to a band shift of $\approx 3.5 \text{ cm}^{-1}$, similar to the values observed experimentally (13).

Low Temperature and High Temperature Gas Phase FT-IR Spectra of C_{70} Fullerene

In the case of C_{70} , because of its lower D_{5h} symmetry, there are five kinds of nonequivalent atomic sites and eight kinds of nonequivalent bonds. This means that the number of normal vibrations increases for C_{70} in comparison to C_{60} . Although there are now 204 vibrational degrees of freedom for the 70-atom molecule, the symmetry of C_{70} gives rise to a number of degenerate modes so that only 122 modes are expected. Of these 31 are infrared-active and 53 are Raman-active (1,2).

Owing to the elongated form and reduced symmetry of C_{70} molecule, the orientational transition and crystal phases are more complicated than in C_{60} . A variety of measurements have shown that C_{70} crystal can be prepared in either f.c.c. or hexagonal, close-packed h.c.p. form. Since the two forms are almost isoenergetic, they can co-exist under determinate conditions. The transition from a fully disordered phase to a partially ordered phase occurs at 337 K, but the low temperature ordered phase can be reached at 276 K (14). Another transition in C_{70} occurs at 200 K.

In Figure 5 are reported two FT-IR spectra of C_{70} recorded, respectively, at 93 K and 523 K as in the previous case of C_{60} . In the wavelength (μm) abscissa scale it is difficult to appreciate the band shift due to temperature change occurred in C_{70} embedded in KBr. Therefore, Figures 6 and 7 show the details of the spectra in wave numbers putting in evidence the small band shift measured at the two temperatures employed.

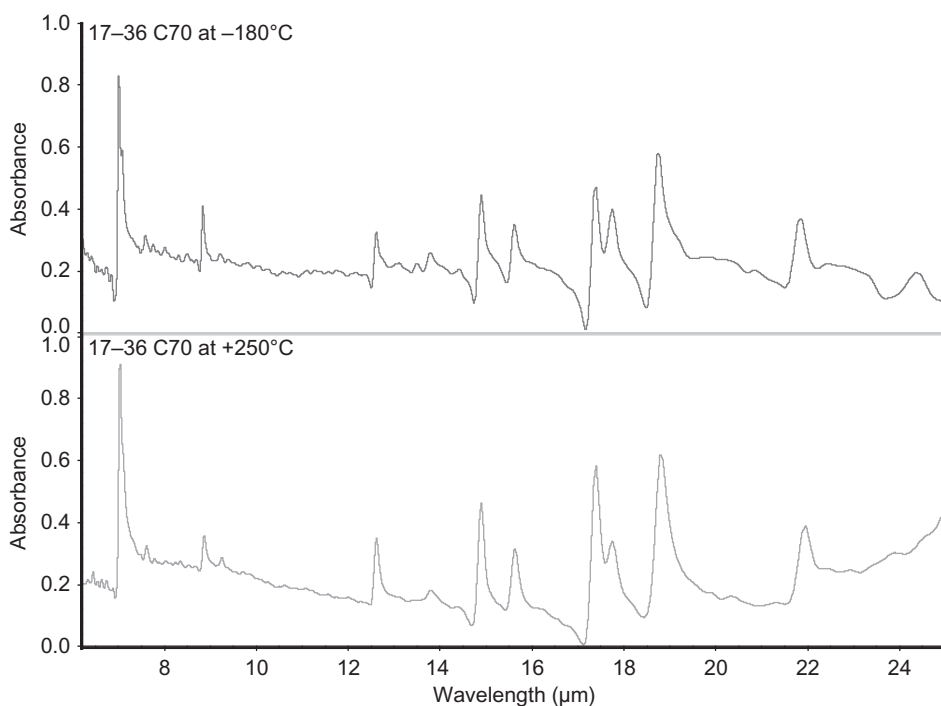


Figure 5. The FT-IR spectrum of C_{70} (in KBr). The spectrum at the top of the figure was registered at 93 K (-180°C) and 523 K ($+250^\circ\text{C}$) at the bottom of the figure.

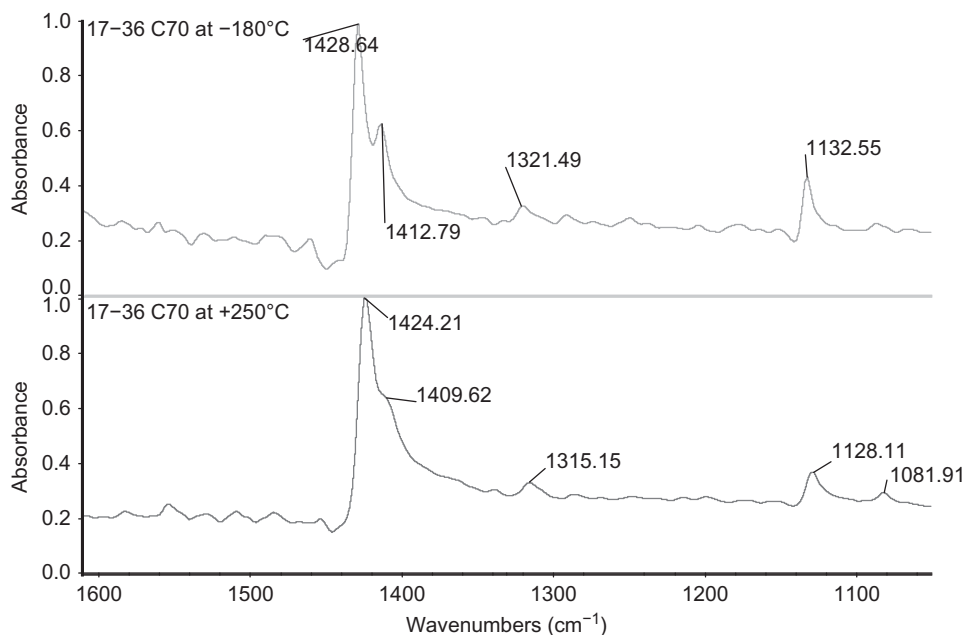


Figure 6. Detail of the FT-IR spectrum of C₇₀ in KBr in the range between 6.25 μm (1600 cm⁻¹) and 9.52 μm (1050 cm⁻¹) taken at 93 K (-180°C) and 523 K (+250°C).

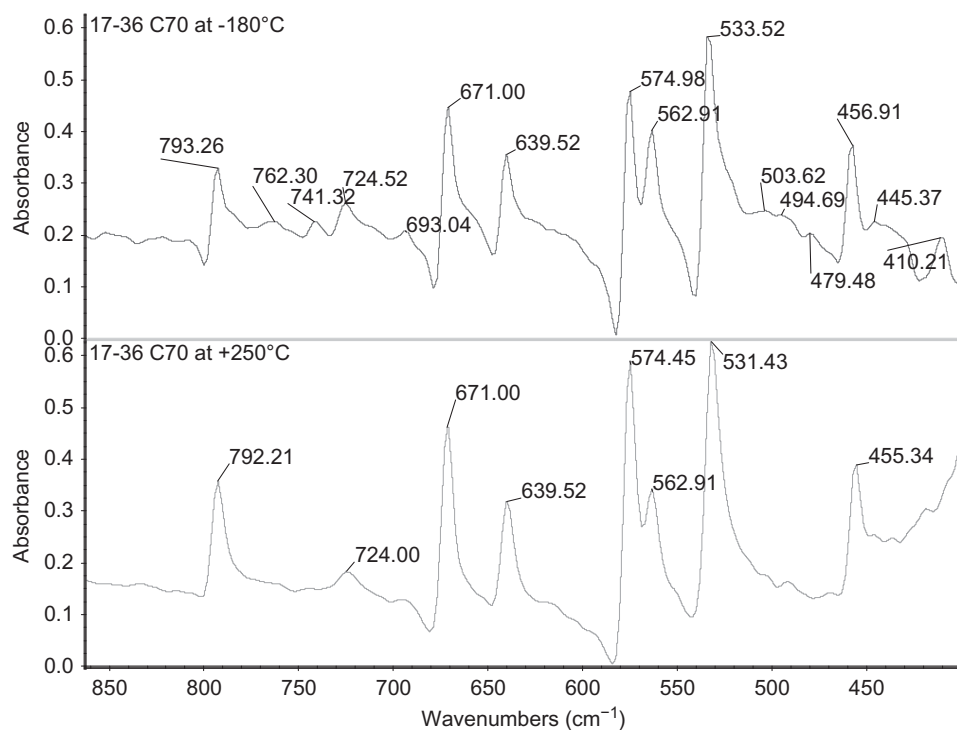


Figure 7. FT-IR spectrum of C₇₀ in KBr taken at -180°C and +250°C detail in the range between 11.11 μm (900 cm⁻¹) and 25.00 μm (400 cm⁻¹).

Table 2
Summary of C₇₀ infrared absorption bands and width (fwhm in parenthesis) in cm⁻¹

0 K (*) KBr matrix extrap. to 0 K	0 K (**) gas phase extrap. to 0 K	0 K gas/KBr difference	93 K (*) KBr matrix	523 K (*) KBr matrix	1083 K KBr matrix extrap. to 1083 K	1083 K (**) gas phase	1083 K (**) gas phase emission	1083 K gas/KBr difference
1429.6	1432.0	2.4	1428.6	1424.2	1418.5	1411.8 (18.2)	1411.8	6.7
1413.5			1412.8	1409.6	1405.5			
1322.9			1321.5	1315.1	1306.8			
1133.5	1144.1	10.6	1132.5	1128.1	1122.4	1121.7 (14.7)	1122.2	0.2
1085.8	1099.6	13.8	1085.0	1081.2	1076.3	1077	1077.2	-0.9
793.5	793.0	-0.5	793.3	792.2	790.7		793.3	-2.6
724.6			724.5	724.0	723.3			0.0
			671.0	671.0				
	638.0		639.5	639.5		638.5		
	583.1		574.5	574.4		574.9	575.3	
	567.7		562.9	562.9		556.9	553.3	
534.0	545.0	11.0	533.5	531.4	528.6	527.6 (10.0)	528.2	0.4
457.2			456.9	455.3	453.2			

(*) This work.

(**) From ref. (12).

As already observed for C_{60} , by passing from high (523 K) to low temperatures (93 K), there is a systematic shift of the vibrational bands to higher frequencies, although there are also bands that appear completely insensitive to the temperature change. For C_{60} , an example of infrared band not sensitive to temperature change, at least in KBr matrix is that at 524 cm^{-1} (see Table 1). As shown in Table 2, a similar phenomenon can be observed also in the infrared spectra of C_{70} where a series of vibrational absorption bands are quite insensitive to the temperature change of the sample in KBr matrix. However, there are also other vibrational bands of C_{70} whose frequency is depended on the temperature, and this has allowed us to extrapolate their position at 0 K. The results of such extrapolations are reported in Table 2 in comparison with the data concerning the C_{70} absorption bands extrapolated to 0 K from gas phase infrared spectral data taken from Nemes et al. (12). As expected, in both cases the temperature-sensitive bands tend to shift to the highest possible frequencies, and the shift appears more pronounced with the extrapolation from the gas phase data rather than for the data taken in KBr. This is certainly due to a matrix effect.

The infrared vibrational frequencies of C_{70} taken in KBr matrix in the range between 93 K and 523 K were also extrapolated to very high temperature, that is, 1083 K, and compared with the gas phase spectrum of C_{70} from literature data (12). High temperature causes a shift toward lower frequencies and band broadening. Surprisingly, in this case the agreement between the infrared peak position taken from C_{70} in KBr matrix and extrapolated to 1083 K shows a general good agreement with the experimental spectrum measured on C_{70} in the gas phase. Another interesting aspect reported in Table 2 regards the fact that the emission infrared band position of the C_{70} in the gas phase are almost coincident with the absorption bands (12).

Conclusion

The infrared absorption spectra of C_{60} and C_{70} have been recorded in KBr matrix at 93 K and were extrapolated to 0 K and above 1000 K. The results of such extrapolation have been compared with gas phase spectral data taken on C_{60} and C_{70} above 1000 K and extrapolated to 0 K. The entity of the matrix effect exerted by KBr has been quantified both at 0 K and at 1000 K.

The approach to measure the band shift on a sample embedded in KBr matrix in the temperature range between 93 K and 523 K and then extrapolate the trend to 0K and to $>1000\text{K}$ has been proved to give reasonably good results in agreement with experimental results and with results obtained from extrapolation of the gas phase spectra provided that the matrix effect exerted by the KBr embedding the sample under analysis was taken into account.

Acknowledgments

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