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Rapid note

Resonant two-photon ionisation spectroscopy of C_{60}

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Abstract. The electronic absorption spectrum of C_{60} has been measured using a continuous gas phase source which is capable of cooling the molecules to a vibrational temperature below ca. 100 K. The results are in good agreement with a previous high resolution gas phase spectrum reported for the spectral range 595 nm–630 nm, obtained with a pulsed Smalley source [1]. The spectral range down to 450 nm is reported for the first time for a molecular beam expansion and is compared with published spectra obtained in solution [2].

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Much theoretical effort has gone into predicting the electronic states and spectroscopy of C_{60} [3–6]. There has also been a great deal of experimental work carried out, mainly for spectroscopy in solution at room temperature [7–9] but also at low temperatures [2,10], in pure C_{60} films [11,12], in single crystal and glassy matrices [13] or in gas cells [14]. More recently, spectroscopy of fullerenes imbedded in rare gas matrices [15] has been reported which has the advantage of cooling the fullerenes down to very low temperatures in an inert medium and enables considerable detail to be obtained. There are also very recent results on the absorption spectrosopy of C_{60} molecules embedded in He clusters where there is significantly less interaction with the surrounding medium than in standard matrix spectroscopy [16].

However, in order to fully understand the electronic properties of the isolated molecule and to determine the effects of solvent and matrix interaction it is essential to have high resolution spectra of gas phase fullerenes. The gas cell experiments have been carried out at temperatures of 800–1000 K, due to the relatively low vapour pressure of C_{60}, and produce spectra with a resolution comparable to that of the solution spectra [2]. There is only one report in the literature of high resolution gas phase spectra which covers the spectral ranges from 595–635 nm and 380–410 nm [1]. This pioneering work from the Smalley group used a 'Smalley source' in which fullerenes were laser desorbed and cooled by a molecular beam expansion in He carrier gas.

In spite of the importance of producing such high resolution spectra, and the efforts of a number of groups worldwide, this data has not been reproduced or expanded upon in the succeeding years. The problem is the high vapourisation temperature of C_{60}, as mentioned above, and the correspondingly high degree of vibrational excitations in the molecular beam which are only cooled with difficulty by standard pulsed nozzle gas expansions.

In this rapid note we report the first high resolution spectroscopy measurements on gas phase C_{60} produced with a continuous molecular beam source which is capable of cooling the vibrational temperature of the molecules in the beam to a value of less than 100 K.

The source is based on a cluster aggregation type source of the kind used by T.P. Martin et al. [17] and Haberland et al. [18]. We have previously used this source to produce and study clusters of fullerenes [19]. An upper limit for the vibrational temperature in the beam could be estimated from a consideration of the dimer binding energy and the flight-time through our source [20]. By reducing the temperature of the fullerene oven in the source, and thus greatly reducing the density of fullerenes in the gas phase, it is possible to avoid the production of clusters. This makes the study of the gas phase properties of vibrationally cold, isolated C_{60} possible.

We use a similar setup for resonant two-photon ionisation as originally used by Haufler et al. [1]. This utilises the electronic energy retained after intersystem crossing to the triplet manifold. A tunable Nd:YAG pumped MOPO with a fluence of typically $50\mathrm{mJ/cm^2}$ and a pulse length of 5–10 ns was used to excite C_{60}. There was then a delay of 2 μs, allowing ample time for the system to cross to the triplet manifold from where it was single-photon ionised with an ArF laser (193 nm, $h\nu$ = 6.4 eV) with a fluence on the order of 100 $\mu J/\mathrm{cm^2}$ and pulse length 10–20 ns. Care was taken to minimise multiple photon absorption from each laser and no such was found for the MOPO alone. The finite background present from the ArF laser alone was measured before and after each scan and subtracted. The ion signals were averaged over 300–500 shots per wavelength and scan. Scans were repeated an average of three times. The wavelength was calibrated with a wavemeter.

Table 1. Assignment of the resonant 2-photon ionisation spectrum (cm^{-1}) from a cold molecular beam. The peakpositions have been fitted using gaussian peak shapes

Present	from [1]	*assignment*	ν^a	ν^b	ν^c
16728	16751	$G_g + h_u(4) + h_g(1)$[d]	16730	16713	16730
16711	16734	$G_g + t_{2u}(1) + h_g(1)$	16708	16679	16705
16681	16702	$T_{1g} + h_u(4) + h_g(1)$[e]	16674	16656	16673
–	16679	–	-	-	-
16636	16658	$T_{2g} + g_u(4)$	16648	16692	16660
–	16647	–	-	-	-
–	16615	–	-	-	-
–	16578	–	-	-	-
–	16563	$G_g + g_u(3)$	-	16564	16514
–	16539	–	-	-	-
16518	16514	$G_g + g_u(2)$[d]	16489	16548	16480
–	16493	–	-	-	-
16477	16470	$G_g + h_u(4)$[d]	16470	16456	16473
16453	16455	$G_g + t_{2u}(2)$	16447	16422	16448
16412	16408	$G_g + h_u(3)$[d]	16399	16544	16394
16345	16350	$T_{2g} + h_u(3)$[e]	16352	16497	16374
16295	16295	–	-	-	-
16268	16261	$G_g + h_u(2)$[d]	16257	16263	16262
16232	16228	–	-	-	-
16209	16207	$T_{1g} + t_{1u}(1)$	16205	16224	16207
–	16080	$G_g + g_u(1)$[d]	16077	16090	16081
–	16080	$T_{2g} + h_u(1)$	16088	16088	16084
–	16035	$T_{2g} + g_u(1)$[e]	16030	16043	16034

[a] Calculated with experimental frequencies from [22] with reassignments proposed in [6]
[b] Calculated with theoretical frequencies from [5]
[c] Calculated with theoretical frequencies from [23]
[d] Same assignment as [6]
[e] Different assignment from [6]

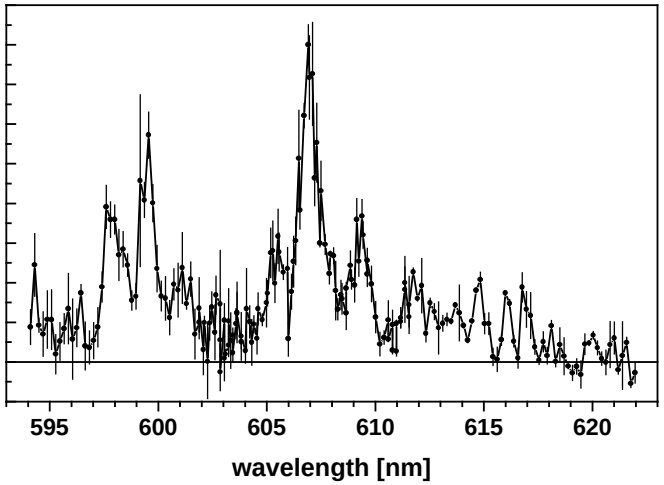

Fig. 1. High resolution resonant two-photon ionisation spectrum of C_{60} from the cold molecular beam source. The *horizontal line* is the zero absorption baseline

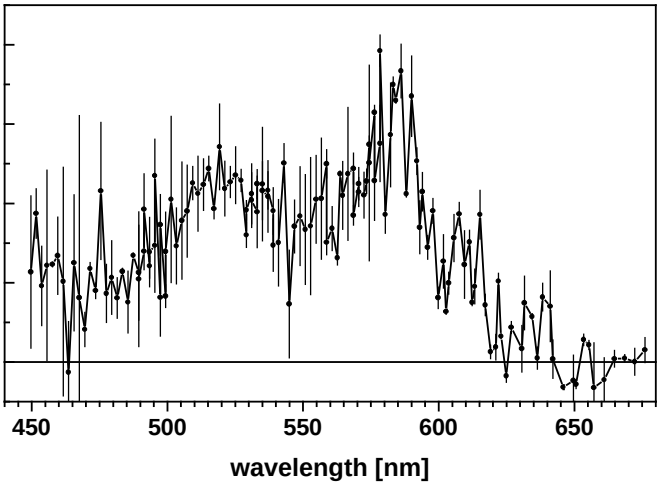

Fig. 2. Coarse-grained abosrption spectrum of C_{60}. The scan step is 2–3 nm, much higher than the resolution. The relative smoothness below of the absorption profile below 580 nm suggests a quasi-continuum in that region

Figure 1 shows the spectrum obtained in the wavelength region of 594–620 nm which was also covered by the original Smalley experiment [1]. The resolution was somewhat poorer in our experiments due to the width of the laser line (10 cm^{-1}) and a mode instability of similar magnitude but the main features can be seen very clearly and are in very good agreement with the results from Haufler et al. [1] as shown in Table 1. The only deviation may be at the blue end of the spectrum where we have a consistent shift of ca. 20 cm^{-1} to the red.

The most intense bands in the spectrum obtained by Haufler et al. have been assigned previously to the G_g state while the two weak bands at 623.8 and 611.7 nm were assigned to the T_{1g} state [6]. Most of the low intensity features seen in the Haufler et al. spectrum have counterparts in our spectrum and would thus appear to be genuine. We even observe some signal in the range 601–605 nm where a number of small but clearly defined peaks can be seen in the Haufler spectrum.

Unfortunately our signal is not good enough to resolve these structures but we also believe them to be genuine.

We have assigned the peaks in the two gas phase spectra based on the calculations of oscillator strength by Negri et al. [21]. The assignment is slightly different than that given previously but we believe it to be in better agreement with the oscillator strength calculations [21] and the estimates of the gas phase origins for the three contributing states, G_g, T_{1g} and T_{2g}, given by Sassara et al. [15]. We have also compared the observed frequencies with the experimental values obtained by Schettino et al., based on crystal Raman and IR spectra [22], and the calculations of Negri et al. [5] and Gianozzi and Baroni [23]. As has been seen before [6] the DFT calculations of Gianozzi and Baroni [23] give rather better agreement with experiment than the QCFF/PI calculations of Negri et al. [5]. We assumed the highest peak to be due to the $G_g + h_u(4)$ transition as indicated by the oscillator strength calculations and, using the experimental value of 738 cm^{-1} for $h_u(4)$ [22], fixed the G_g origin to lie at 15732 cm^{-1}. The T_{2g} origin was assumed to lie at 15685 cm^{-1} and the T_{1g} origin at 15680 cm^{-1}. The main differences compared to the previous assignment [6] are that we assign three transitions to the T_{2g} state and have changed the assignment of the relatively intense peak seen at 16681 cm^{-1} (16702 cm^{-1} in [1]) to a combination band of the T_{1g} state rather than $G_g + g_u(4)$ which is predicted to have zero oscillator strength [21].

A more coarse-grained wavelength scan of the region down to 450 nm (22222 cm^{-1}) is shown in Fig. 2.

This was obtained by scanning the laser and collecting a mass spectrum every 2–3 nm. All the main features observed in solution spectra [2] can be seen here but shifted by approximately 15–20 nm to the blue (ca. 570 cm^{-1} for the γ states at around 580 nm increasing to ca. 700 cm^{-1} for the δ states at around 520 nm). The solution spectra are expected to be red shifted compared to the gas phase spectra due to intermolecular interactions. This has also been observed, but with a somewhat smaller shift, in the high temperature gas phase absorption spectra [14].

Obviously, there are still many questions to be answered concerning the correct assignment and understanding of the highly complex spectra observed from C_{60} under different conditions. The interpretation has been made very difficult due to the sparcity of high resolution gas phase data available up to now. With the preliminary results presented here we have confirmed the gas phase spectra measured by Haufler et al. [1] and are now in the position of carrying out very necessary detailed studies over a large spectral range with a stable continuous molecular beam source providing a vibrational temperature on the order of 100 K.

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