Gas-phase Absorption of C$_{70}^{2+}$ Below 10 K: Astronomical Implications

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Abstract

The electronic spectrum of the fullerene dication C$_{70}^{2+}$ has been measured in the gas phase at low temperature in a cryogenic radiofrequency ion trap. The spectrum consists of a strong origin band at 7030 Å and two weaker features to higher energy. The bands have FWHMs of 35 Å indicating an excited state lifetime on the order of one-tenth of a picosecond. Absorption cross-section measurements yield $(2 \pm 1) \times 10^{-15}$ cm^2 at 7030 Å. These results are used to predict the depth of diffuse interstellar bands (DIBs) due to the absorption by C$_{70}^{2+}$. At an assumed column density of 2×10^{12} cm^{-2} the attenuation of starlight at 7030 Å is around 0.4% and thus the detection of such a shallow and broad interstellar band would be difficult. The electronic spectrum of C$_{60}^{2+}$ shows no absorptions in the visible. Below 4000 Å the spectra of C$_{60}$, C$_{60}^{+}$ and C$_{60}^{2+}$ are similar. The large intrinsic FWHM of the features in this region, $\sim$200 Å for the band near 3250 Å, make them unsuitable for DIB detection.

Key words: ISM: molecules

1. Introduction

In 2015, gas-phase laboratory spectroscopy led to the confirmation that two near-infrared diffuse interstellar bands (DIBs) at 9577 and 9632 Å are due to absorption by the molecular ion C$_{60}^{+}$ (Campbell et al. 2015). This study followed the first observation of these features in diffuse clouds by Foing & Ehrenfreund (1994), whose astronomical search was based on the matrix isolation spectroscopy results of Fulara et al. (1993). More recently, the gas-phase laboratory spectrum was revisited and more accurate limits were placed on the wavelengths of the C$_{60}^{+}$ bands. These were also compared to the complete set of astronomical data reported in the literature hitherto (Campbell et al. 2016b).

The two strong interstellar bands at 9577 and 9632 Å are responsible for $\sim$10% attenuation in the intensity of starlight in observations toward the star HD 183143 (Walker et al. 2015). The results of combined laboratory and astronomical studies have led to the direct determination of the C$_{60}^{+}$ column density (Campbell et al. 2016a) in the line of sight toward HD 183143, $N(\mathrm{C}_{60}^{+}) = (2.0 \pm 0.8) \times 10^{13}$ cm^{-2}, which is similar to the abundance of diatomics such as CH^{+} (McCall et al. 2002). Three weaker absorption bands in the C$_{60}^{+}$ laboratory spectrum have now also been detected as DIBs (Walker et al. 2015; Campbell et al. 2016a; Walker et al. 2016).

The column densities of much smaller (di- and triatomic) species present in diffuse clouds decrease sharply with increasing molecular size (Snow & McCall 2006). This observation, together with the relatively high value for C$_{60}^{+}$, has renewed interest in so-called top down chemistry (Oka & Witt 2016). In such a scenario, the abundance of molecules is governed by their ability to withstand decomposition in the $\sim$10^7 year lifetime of diffuse clouds. The fullerenes are well known to be remarkably stable against destructive processes and the electronic spectra of other members of the family are therefore sought.

Shortly after the confirmation of C$_{60}^{+}$ in the interstellar medium, the gas-phase electronic spectrum of C$_{70}^{+}$ was presented (Campbell et al. 2016a). The intensity of the electronic transition of the latter, while in the spectral region

of interest for the DIBs, is rather evenly distributed among more than 20 vibronic bands. As a result, even if the column density of C$_{70}^{+}$ were to be the same as for C$_{60}^{+}$, it would still not be detectable with current ground-based telescopes. O$_2$ absorption in the Earth's atmosphere obscures the range of wavelengths from 7600 to 7660 Å, where some of the strongest C$_{70}^{+}$ features are found, making ground-based astronomical searches for bands of predicted <1% depth even more challenging. With more conservative estimates of the C$_{70}^{+}$ column density, e.g., 10% of $N(\mathrm{C}_{60}^{+})$ as is typically seen in laser vaporization fullerene synthesis (Kroto et al. 1985), the prospect of detecting C$_{70}^{+}$ through this electronic transition becomes even worse. However, given that neutral C$_{70}$ was observed in the young planetary nebula Tc 1 (Cami et al. 2010), one might also expect the ionized form to be present in the interstellar medium. The IR emission spectrum from Tc 1 suggests that C$_{60}$ is eight times more abundant than C$_{70}$ in this environment; this value is judged to be uncertain by around a factor of two (J. Cami 2016, private communication).

The ionization potential (IP) of C$_{60}^{+}$ is 11.5 eV (Wörgötter et al. 1994), which is below the 13.6 eV threshold energy for interstellar photons. It is therefore possible, on energetic grounds at least, that ionization of C$_{60}^{+}$ takes place in regions exposed to a strong UV radiation field. A similar situation must prevail for C$_{70}^{+}$, which has an IP of 11.4 eV. Therefore, the electronic spectra of doubly charged fullerenes are also of potential interest in the context of the DIBs.

In the following, the gas-phase electronic spectrum of C$_{70}^{2+}$ in the red part of the visible is presented. In addition, measurements of absolute absorption cross-sections are reported and the astronomical implications for the detection of this dication are discussed. Unlike C$_{70}^{2+}$, C$_{60}^{2+}$ possesses no absorptions in the visible (Kern et al. 2014). The characteristics of the electronic spectra of C$_{60}$, C$_{60}^{+}$, and C$_{60}^{2+}$ in the UV region are also discussed in the context of their astronomical detectability.

2. Experimental

Experiments were performed with the cryogenic ion trapping apparatus described in Campbell et al. (2016a). Singly and
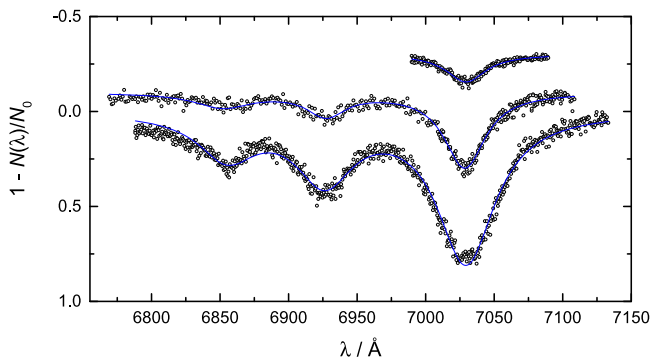
Figure 1. Gas-phase electronic absorption spectrum of C_{70}^{2+} below 10 K, measured by photofragmentation of $C_{70}^{2+} - He$ complexes stored in a cryogenic radiofrequency ion trap. Experimental data (circles) have been fit with three Lorentzian functions, the cumulative profiles are the blue lines. Vertical offsets have been applied to the data obtained using laser fluences of $\sim 210 \, \mu J \, cm^{-2}$ (bottom), $65 \, \mu J \, cm^{-2}$ (middle), and $15 \, \mu J \, cm^{-2}$ (top). The width of the bands recorded with $1 - N(\lambda)/N_0 \geqslant 0.1$ show a saturation broadening.

doubly charged fullerene cations were produced by 50 eV electron bombardment of the neutral gas, produced by heating a solid C_{60}/C_{70} sample to 350/450°C. After passing through a quadrupole mass filter, the ions are turned by 90° and injected into a linear quadrupole ion trap ($r_0 = 5 \, mm$, $V_0 = 150 \, V$, $f = 780 \, kHz$). The trap is mounted on the second stage of a closed cycle helium cryostat, where the temperature of the walls is below 5 K. The ions are cooled via collisions with helium buffer gas that is introduced into the trap using a piezo valve. At these low temperatures and with high buffer gas number densities present (some $10^{15} \, cm^{-3}$), weakly bound ion-helium complexes are formed. The gas is pumped out for several hundred milliseconds and the complexes interact with laser radiation produced by a pulsed Nd:YAG pumped dye laser (0.02 Å bandwidth). After irradiation, the trap contents are emptied and analyzed using a quadrupole mass spectrometer and a Daly detector. The wavelengths of the $C_{70}^{2+} - He$ absorption bands will be shifted from those of C_{70}^{2+} due to the presence of the helium atom. This effect is expected to be small as similar experiments (Campbell et al. 2016a) on $C_{70}^+ - He$ have shown (~ 0.4 Å), especially considering the ~ 35 Å FWHM of the C_{70}^{2+} absorption (see Section 3).

Absolute cross-sections are determined by monitoring the number of ions as a function of the laser fluence Φ to which they are exposed. Experiments were made using a single pulse of a flat top profile (3.2 mm diameter) dye laser. The number of complexes follows the exponential function $N(\Phi) = N_0 \exp(-\Phi/\Phi_0)$. The cross-section is obtained from the derived characteristic fluence, Φ_0 [mJ per cm^2], and the photon energy, $h\nu$ [mJ], via $\sigma = h\nu/\Phi_0$ [cm^2].

3. Electronic Spectrum of C_{70}^{2+} in the Range of 6800–7100 Å

The absorption spectrum recorded by photofragmentation of $C_{70}^{2+} - He$ is presented in Figure 1. The origin band of the electronic transition is at 7030 Å and has an FWHM of approximately 35 Å. Two additional absorption bands of weaker intensity are observed at 6927 and 6857 Å. The energy separation of these from the origin, $210 \, cm^{-1}$ and $370 \, cm^{-1}$, respectively, is consistent with the excitation of low-frequency vibrational modes in the excited electronic state that are typical of the fullerenes. The bands are well represented by a
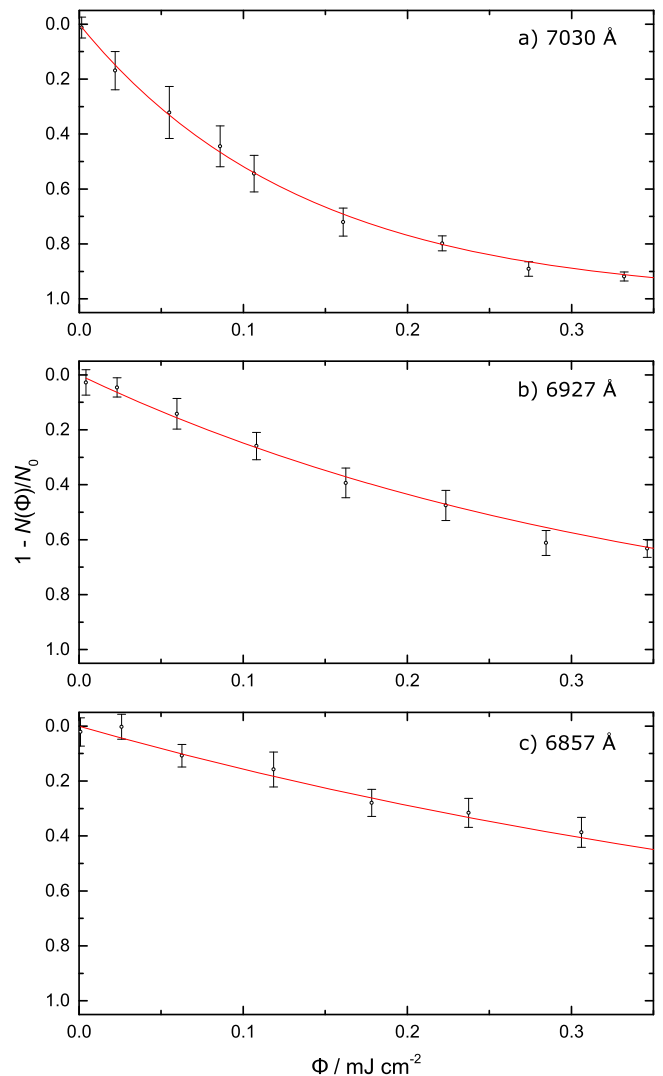

Figure 2. Fragmentation of $C_{70}^{2+} - He$ as a function of laser fluence at wavelengths of (a) 7030 Å, (b) 6927 Å, and (c) 6857 Å. The experimental data (circles) have been fit with exponential functions (lines), providing information on the photofragmentation cross-sections. The data have been corrected for background ions appearing at $m/z = 422 \, u/e$.

Lorentzian function and their FWHM imply an excited state lifetime on the order of one-tenth of a picosecond.

This transition of C_{70}^{2+} has been observed in a low-temperature matrix isolation study (Kern 2015). The absorption of C_{70}^{2+} is also evident in the study of C_{70}^+ (Fulara et al. 1993) though it was assumed to belong to C_{70}^+. The experimental scheme used (Fulara et al. 1993) to produce C_{70}^+ involved irradiation of a matrix containing neutral C_{70} with 16.8 eV photons. Because the IP of C_{70}^+ is 11.4 eV (Wörgötter et al. 1994), it appears that doubly charged species were also formed. Based on TD-DFT calculations and IR spectra, it has been assigned as $4 \, {}^3E_1' \leftarrow X \, {}^3A_1'$ in D_{5d} symmetry (Kern 2015).

Absorption cross-section measurements in the gas phase were made at the wavelength of the band maxima for each of the three features shown in Figure 1. Typical data are presented in Figure 2. Exponential fits allow the determination of the characteristic fluence, Φ_0, which is found to be $140 \, \mu J \, cm^{-2}$, $350 \, \mu J \, cm^{-2}$, $560 \, \mu J \, cm^{-2}$ at 7030 Å, 6927 Å, and 6857 Å, respectively, implying absorption cross-sections of $(2 \pm 1) \times 10^{-15} \, cm^2$, $(8 \pm 3) \times 10^{-16} \, cm^2$, and $(5 \pm 2) \times 10^{-16} \, cm^2$.

In the context of the abundance of C_{70}^{2+} in diffuse clouds, it is instructive to consider the ratio of ionization cross-sections for the production of singly and doubly charged fullerenes. The electron impact ionization cross-sections for the processes $C_{60} \rightarrow C_{60}^{+}$ and $C_{60}^{+} \rightarrow C_{60}^{2+}$ are similar at 20 eV, with a ratio of ~1.4:1.0 (Matt et al. 1999). Under the assumption that the column density of C_{70}^{+} is between 6% and 25% of $N(C_{60}^{+})$, as estimated from the abundance of the corresponding neutral species detected in Tc 1, $N(C_{70}^{+}) = (1.2 - 5.0) \times 10^{12}$ cm^{-2}. Assuming further that the $N(C_{70}^{+})$: $N(C_{70}^{2+})$ ratio is solely determined by the above ionization cross-sections, $N(C_{70}^{2+}) = (0.9 - 3.6) \times 10^{12}$ cm^{-2}. At these column densities, the expected depth in the astronomical spectrum at 7030 Å is between 0.2% and 0.7%. These values, together with an FWHM of 35 Å, correspond to equivalent widths (EW) of 100 mÅ and 400 mÅ, respectively. It should be noted that, despite these large EWs, the expected shallow absorption (<1% depth) due to the broad profile makes astronomical detection difficult. As discussed by Hobbs et al. (2008), the systematic errors arising from continuum line setting will increase with DIB FWHM.

It is worth emphasizing that there are several uncertainties concerning the above estimate of $N(C_{70}^{2+})$. First, the photoionization cross-sections at energies below 13.6 eV may be different from the above electron impact values. For example, recent photoionization experiments using synchrotron radiation suggest similar cross-sections for the ionization of C_{60} and C_{60}^{+} (Douix et al. 2017) and the same result may hold for C_{70}. However, because the 11.4 eV IP of C_{70}^{+} is close to the 13.6 eV threshold, one might anticipate a slower rate for $C_{70}^{+} + h\nu \rightarrow C_{70}^{2+} + e^{-}$ than for the process $C_{70} + h\nu \rightarrow C_{70}^{+} + e^{-}$ because only a narrower range of interstellar photon energies can contribute. In addition to photoionization, the electron recombination rates for these species are unknown. Such uncertainties have recently been discussed by Omont (2016).

4. On the UV-vis Spectra of Neutral and Charged Fullerenes

The absorption spectra of neutral, positive and negative, and doubly charged fullerene ions all display broad absorptions in the UV from 2000 to 4000 Å. These high-energy absorption bands have been described as plasmon-type resonances and are thus similar for the different charge states possible for a particular fullerene (Kern et al. 2014). Low-temperature matrix isolation spectra have been presented for C_{60}^{-}, C_{60}, C_{60}^{+}, C_{60}^{2+}, and C_{60}^{3+} (Kern et al. 2014; Strelnikov et al. 2015), in addition to the spectra of the corresponding species containing 70 carbon atoms (Kern et al. 2016). The search for interstellar neutral C_{60} absorptions in this spectral range has been described by Sassara et al. (2001).

The UV absorptions have large oscillator strengths but are very broad. For example, the C_{60} band around 3250 Å has an FWHM of ~200 Å (Kern et al. 2014). The latter is similar in solution, at high temperature in the gas phase and in low-temperature matrix isolation spectra (see Sassara et al. 2001 and references therein). A comparable FWHM is observed by us for C_{60}^{+} and C_{60}^{2+} below 10 K by the fragmentation of helium complexes stored in the cryogenic trap using a pulsed optical parametric oscillator (OPO) with a 1 Å bandwidth. This suggests that the FWHM is determined by the lifetime and/or congestion of excited vibronic state(s). The

absorption cross-section of the C_{60} band at 3300 Å has been reported as 1.5×10^{-16} cm^2 (Smith 1996) and a similar value is expected for C_{60}^{+}. The depth of the corresponding absorption in the astronomical spectrum of C_{60}^{+} with a column density of 2×10^{13} cm^{-2} would be only 0.3%. Astronomical detection of such a broad and shallow absorption represents a significant challenge.

As a result of the non-detection of an interstellar C_{60} absorption in this region, Herbig (2000) put an upper limit of 4.5×10^{11} cm^{-2} on its column density. However, this estimate was based on a search for a feature with an assumed FWHM of only 1 Å. He did state that much broader bands, with FWHMs that are two orders of magnitude larger, would not be detectable and thus the $N(C_{60})$ estimate is invalid (Herbig 2000). The lack of an upper limit on the column density of neutral C_{60} means that the degree of ionization in diffuse clouds is uncertain.

The 13.6 eV threshold energy for interstellar photons is above the ionization energy of C_{60}^{+}. Removal of an electron from C_{60}^{+} can lead to either a triplet or singlet C_{60}^{2+} ground electronic state in D_{5d} symmetry, the latter being the lowest energy, and only weak absorptions are predicted for the singlet (Kern et al. 2014). Electronic spectra of C_{60}^{2+} in a neon matrix reported by the same authors showed no absorptions in the range of 8000–10500 Å. We scanned this spectral region with a tunable OPO; however, no absorptions were observed.

5. Conclusions

The characteristics of the C_{70}^{2+} gas-phase spectrum presented here are of relevance to the question concerning the role played by fullerenes other than C_{60}^{+} with respect to the DIBs. This is because the intensity of the transition is not spread over many vibronic bands of similar strength, such as in the case of the $^2E_1' \leftarrow X\ ^2E_1''$ band of C_{70}^{+} (Campbell et al. 2016a). The dilution of the electronic band oscillator strength over more than 20 absorptions in the latter precludes astronomical detection currently. The C_{70}^{2+} spectrum, on the other hand, is much less congested and the majority of the oscillator strength is contained within one or two absorption bands. In this respect, it is similar to the NIR spectrum of C_{60}^{+} (Campbell et al. 2015), however, the large FWHM of the C_{70}^{2+} bands, caused by the short excited state lifetime, make astronomical searches difficult.

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