Although fullerenes have long been hypothesized to occur in interstellar environments, they have only recently been unambiguously identified through spectroscopy\textsuperscript{14}. \textit{C}_{60+}, \textit{C}_{70} and \textit{C}_{60}+ now constitute the largest molecular species individually identified in the interstellar medium. Fullerenes have substantial proton affinities and it has been suggested that \textit{C}_{60}H\textsuperscript{+} is likely the most abundant interstellar analogue of \textit{C}_{60} (ref. 1). We present here a laboratory infrared (IR) spectrum of gaseous \textit{C}_{60}H\textsuperscript{+}. Symmetry breaking in \textit{C}_{60}H\textsuperscript{+} produces an IR spectrum that is much richer than that of \textit{C}_{60}. The experimental spectrum is used to benchmark theoretical spectra indicating that the B3LYP density functional with the 6-311+G(d,p) basis set accurately reproduces the spectrum. Comparison with IR emission spectra from two planetary nebulae, SMP LMC\textsuperscript{56} and SMC\textsuperscript{16}, which have been associated with high \textit{C}_{60} abundances, indicates that \textit{C}_{60}H\textsuperscript{+} is a plausible contributor to their IR emission.

Buckminsterfullerene \textit{C}_{60} is undoubtedly one of the most iconic molecules of our time. Since its discovery in 1985\textsuperscript{6}, its physicochemical properties have been extensively characterized, including its ion chemistry and spectroscopic properties. IR spectra have been reported in condensed and gas phases\textsuperscript{10,16}, and spectra for ionized forms are available as well\textsuperscript{14,16,17,18}.

The high cosmic abundance of carbon combined with the high stability of fullerenes\textsuperscript{11} initiated a quest for their detection in interstellar environments.\textsuperscript{14-17} This search culminated in the identifications of neutral \textit{C}_{60} and \textit{C}_{70} in a young planetary nebulae (Tc1) based on diagnostic IR features. Accurate gas-phase laboratory spectra in the near-IR range led to the identification of \textit{C}_{60}H\textsuperscript{+} as carrier of two of the diffuse interstellar bands near 9600 Å (ref. 1). However, to our knowledge, no IR spectra have been reported for protonated fullerenes. Electronic spectra have been suggested to suffer from broad, unresolved features due to tunnelling of \textit{H}\textsuperscript{+} between the identical C-atom sites\textsuperscript{18}. IR spectra have been reported for deposited fullerene films exposed to atomic hydrogen\textsuperscript{19} and for some stable \textit{C}_{60}H\textsubscript{x} hydrogenated fullerenes\textsuperscript{20}.

Here we present an experimental IR spectrum of protonated \textit{C}_{60} recorded in the gas phase via infrared multiple-photon dissociation (IRMPD) using the FELIX free-electron laser and an ion trap mass spectrometer\textsuperscript{21}. This IR spectrum is compared with astronomical spectra of objects that were associated with high \textit{C}_{60} abundances as well as with theoretical IR spectra to evaluate the performance of different computational approaches. Contrasting the spectrum with that of \textit{C}_{60} yields a textbook example of the effects of symmetry breaking on vibrational selection rules.

\textit{C}_{60}H\textsuperscript{+} generated by atmospheric-pressure chemical ionization (APCI) produces the mass spectrum in Fig. 1b, showing the radical cation of \textit{C}_{60} at \textit{m}/\textit{z} 720, clearly resolved from the higher-intensity \textit{m}/\textit{z} 21 at a natural carbon-13 abundance of 1.1%, monoisotopic \textit{\textsuperscript{13}C}_{60} occurs at only 51%, while the \textit{\textsuperscript{13}C}_{2}\textit{\textsuperscript{12}C}_{59} isotopologue has an abundance of 34%. Hence, the \textit{m}/\textit{z} 721 base peak is a superposition of two ions: the protonated ion \textit{C}_{60}H\textsuperscript{+} and the \textit{\textsuperscript{13}C}_{2}\textit{\textsuperscript{12}C}_{59}\textsuperscript{•+} radical cation; the small mass difference of 0.0045 u cannot be resolved in our mass spectrometer. From the observed isotope pattern, the relative populations of \textit{C}_{60}H\textsuperscript{+} and \textit{\textsuperscript{13}C}_{2}\textit{\textsuperscript{12}C}_{59}\textsuperscript{•+} are derived as 65% and 35%, respectively.

Figure 1c shows the mass spectrum after isolation of the \textit{m}/\textit{z} 721 ion in the trap (see Methods). Tuning the laser frequency to a vibrational resonance of \textit{C}_{60}H\textsuperscript{+} leads to the absorption of multiple IR photons, inducing dissociation forming the \textit{m}/\textit{z} 720 ion. Note that only \textit{C}_{60}H\textsuperscript{+} can undergo fragmentation into this channel—by loss of an H atom—while \textit{\textsuperscript{13}C}_{2}\textit{\textsuperscript{12}C}_{59}\textsuperscript{•+} cannot. Moreover, due to its high stability, \textit{C}_{60}\textsuperscript{•+} does not undergo dissociation under our experimental conditions, as was tested by isolating the \textit{m}/\textit{z} 720 ion.

Increasing the number of laser pulses, the \textit{C}_{60}H\textsuperscript{+} population undergoes dissociation until it is depleted. The remaining intensity at \textit{m}/\textit{z} 721 is then exclusively due to \textit{\textsuperscript{13}C}_{2}\textit{\textsuperscript{12}C}_{59}\textsuperscript{•+}. Figure 1d confirms its approximately 35% contribution to the ion population. By monitoring the fragmentation of \textit{m}/\textit{z} 721 into channel \textit{m}/\textit{z} 720 as a function of wavelength, we selectively measure the IRMPD spectrum of \textit{C}_{60}H\textsuperscript{+}, which is not contaminated by contributions from \textit{\textsuperscript{13}C}_{2}\textit{\textsuperscript{12}C}_{59}\textsuperscript{•+}.

Buckminsterfullerene \textit{C}_{60} belongs to theicosahedral point group (I\textsubscript{h})\textsuperscript{10,24}, which leads to IR selection rules that leave the large majority of the 174 normal modes inactive. There are only four triply-degenerate modes belonging to the \textit{T}\textsubscript{1\textscript{g}} irreducible representation that are IR active. As a consequence, \textit{C}_{60} has an extremely sparse IR spectrum, as reproduced in Fig. 2a.
Protonation of aromatic systems occurs through σ -bonding to one of the peripheral C atoms. Protonation of C$_{60}$ is therefore expected to occur on one of the 60 C atoms, and not centrally over one of the five- or six-membered rings. Then, since all C atoms are symmetrically identical, there exists only one isomer of C$_{60}$H$^+$. The C$_{60}$H$^+$ spectrum is compared with that of C$_{60}$ below it. The C$_{60}$H$^+$ spectrum indeed features a significantly larger number of vibrational bands due to symmetry lowering to C$_s$.

Figure 3 compares the experimental spectrum with computed harmonic spectra at various levels of density functional theory (DFT), as further detailed in the Methods. Figure 3 and Supplementary Table 1 clearly testify that the B3LYP/6-311+G(d,p) method outcompetes all others in the prediction of the IR spectrum. The total integrated intensity of all fundamental vibrational modes at this level of theory is 790 km mol$^{-1}$, versus 215 km mol$^{-1}$ for C$_{60}$.

Our statement that there exists only a single isomer of C$_{60}$H$^+$ ignored the—perhaps naive but intriguing—possibility of endohedral protonation, that is, the proton being inside the cage. The optimized geometry is 193 kJ mol$^{-1}$ higher in energy than the exohedrally protonated structure. Moreover, the predicted spectrum is in poorer agreement with the experimental spectrum (Supplementary Fig. 1) and will not be further considered.

Overall, the C$_{60}$H$^+$ spectrum features strong bands in the 1,150–1,570 cm$^{-1}$ (6.4–8.7 μm) range and weaker ones in the long-wavelength range. This general spectral shape resembles that of ionized polycyclic aromatic hydrocarbons (PAHs), but a detailed inspection reveals significant differences (Supplementary Fig. 2). For C$_{60}$H$^+$, the strong bands have mainly C–C stretching character, with some of the vibrations near 1,165 cm$^{-1}$ having additional C–H bending character. For PAHs, the C–C stretch bands extend to shorter wavelengths (6.2 μm). The C$_{60}$H$^+$ bands in the 7.7–8.6 μm range overlap with strong PAH cation bands, but bands to the blue (6.5–7.1 μm) fall in a relatively silent region of the PAH spectrum.

Towards longer wavelengths, the main bands in the PAH spectrum are due to C–H out-of-plane vibrations at 11.3, 12.0 and 12.7 μm. The C$_{60}$H$^+$ spectrum features weak bands near 9.25, 10.45 and 13.15 μm (1,090, 955 and 760 cm$^{-1}$), roughly characterized as ring breathing (9.25 μm) and cage deformation (10.45 and 13.15 μm). Finally, two stronger bands at 17.7 and 19.1 μm (565 and 525 cm$^{-1}$) are close to the two main bands of neutral C$_{60}$ (17.4 and 18.9 μm), with redshifts relative to C$_{60}$ of 10 and 5 cm$^{-1}$, respectively. This is on the order of the bandwidth in the interstellar emission spectra.

C$_{60}$H$^+$ possesses a single C–H stretch mode with a computed integrated intensity of 27 km mol$^{-1}$, which we were unable to detect, probably due to the lower laser power available in this frequency range. As detailed in the Methods, we estimate this band to occur at 2,850 cm$^{-1}$, which deviates from the 100 cm$^{-1}$ broad C–H stretch feature centred at 2,910 cm$^{-1}$ reported for solid hydrogenated fullerences. On the other hand, this position coincides roughly with aliphatic (not aromatic) C–H stretches observed in gas-phase spectra of hydrogenated PAHs. KBr pellet spectra of fulleranes (C$_{60}$H with x ≈ 30) show broad absorption features between 2,800 and 2,940 cm$^{-1}$ (ref. 39).

Since the first spectroscopic identification of C$_{60}$ (ref. 1), various astronomical objects have been particularly associated with high fullerene abundance. Objects with low PAH emission are of particular interest to avoid confusion due to overlapping PAH bands. In Fig. 4, the IR emission spectra of the planetary nebulae SMC16 and LMC36,31 are overlaid onto our laboratory spectrum of C$_{60}$H$^+$ (see also Supplementary Figs. 3 and 4). The two laboratory bands in the 17–20 μm region fall within the bandwidth of the astronomical bands, although they are slightly shifted towards longer wavelengths with respect to the centre position of the astronomical features, overlapping nearly exactly with the two bands in neutral C$_{60}$. The asymmetric lineshape of the astronomical features, with a shoulder towards longer wavelengths, may then be speculated...
to be due to the combined emission from C_{60} and C_{60}H^+. Perhaps most striking is the close correspondence in the 6–9 μm range: the laboratory spectrum falls closely within the envelope in the observational spectra, with some of the individual peaks coinciding remarkably well with partially resolved structures on the envelope. In contrast to the two bands at longer wavelengths, the entire 6–9 μm emission feature cannot be explained by C_{60} alone (dashed lines), nor does it appear to be due to PAHs (Supplementary Fig. 2). The data presented here suggest that a mixture of protonated and neutral C_{60} and higher fullerenes may form a plausible set of carriers for these emission features. A contribution from radical cation fullerenes^8,12,32 is also possible, but requires further investigation. Weaker bands in the remainder of the C_{60}H^+ spectrum are also consistent with the observational data. The 10.45 μm band appears visible in the LMC56 spectrum, and is consistent with the SMC16 spectrum, although overlapped by a broad emission plateau attributed to SiC (ref. 30). Note that relative intensities in emission due to radiative cooling are amplified for bands at longer wavelengths with respect to bands at shorter wavelengths, while in photodissociation spectroscopy this trend is the opposite (see for example Fig. 6 in ref. 23).

The laboratory IR spectrum of C_{60}H^+ overlaid onto emission spectra of objects hypothesized to harbour high abundances of fullerenes appears to be supportive of Kroto’s hypothesis that C_{60}H^+ is abundant. However, C_{60}H^+ alone cannot entirely explain the broad but partially resolved emission feature between 6 and 9 μm in these sources, but neither can available IR spectra of C_{60}\cdot^+ (refs. 8,12,32). We therefore speculate that a mixture of these species and their C_{70} (and perhaps higher fullerene) analogues is currently the most attractive explanation. New spectral data for C_{70}H^+ (currently ongoing in our lab) and C_{70}\cdot^+ are anticipated to further resolve this question. Higher spectral and/or spatial resolution astronomical data from future instruments such as the James Webb Space Telescope may resolve individual contributions more clearly.

Fig. 2 | Experimental IRMPD spectrum of C_{60}H^+ compared with a Fourier transform IR absorption spectrum of a thin film of neutral C_{60} taken from ref. 25. The C_{60} spectrum shows the four IR allowed modes as well as two very weak bands around 1,500 cm\textsuperscript{−1}, which have been attributed to combination modes. The effects of symmetry breaking on the IR selection rules in C_{60}H^+ are striking. Band positions in μm are indicated on the IRMPD spectrum. The stick spectra below the experimental data show the theoretical calculations for both molecules at the B3LYP/6-311+G(d,p) level of theory. Bottom panel adapted from ref. 25, Radboud Univ.
Experiments were performed in a modified three-dimensional quadrupole ion trap mass spectrometer (Bruker Amazon Speed ETD) coupled to the beamline of the Free-Electron Laser for Infrared eXperiments (FELIX). The modifications, including optical access to the trapped ions, have been described in detail in ref. 33.

To produce protonated C\textsubscript{60}, an APCI source was employed, which is particularly efficient for less polar species, such as fullerenes\textsuperscript{34,35} and PAHs\textsuperscript{36,37}.

Fig. 3 | The experimental IR spectrum of C\textsubscript{60}\textsuperscript{H+} compared with DFT computed spectra using different basis sets and functionals.

The experimental spectrum (black) is compared with spectra computed at different levels of DFT (coloured shading). The best match, marked in red, is obtained using the B3LYP functional with the 6-311+G(d,p) basis set. The root mean square deviation between band centres in the experimental spectrum and in the scaled and convoluted theoretical spectra amounts to 1.8 cm\textsuperscript{-1} for this level of theory and is much smaller than for the other computational approaches (see Supplementary Table 1).

Methods

Experiments were performed in a modified three-dimensional quadrupole ion trap mass spectrometer (Bruker Amazon Speed ETD) coupled to the beamline of the Free-Electron Laser for Infrared eXperiments (FELIX). The modifications, including optical access to the trapped ions, have been described in detail in ref. 33.

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Typically, both protonated and radical cation species can be observed from APCI of these species. C\textsubscript{60} (99\%+) was obtained from MER Corporation (USA). The powder was dissolved in toluene to a concentration of 1 mmol, and this stock solution was further diluted in a 50/50% methanol–toluene mixture to provide a final C\textsubscript{60} concentration of about 10\,\mu M. This solution was infused at a flow rate of 8\,\mu l min\textsuperscript{-1}, nebulized with nitrogen at 3.5 bar and 220 °C, and vaporized at 450 °C. The fine droplets were sprayed towards the corona discharge needle. The potential difference between the end plate and capillary was 4,500 V and the corona current was set to 6,000 nA. Ions produced in the APCI source entered the vacuum of the mass spectrometer through a capillary, were guided by the ion-transfer optics and were then trapped in the radio-frequency quadrupole ion trap.

After irradiation of the trapped ion cloud, a mass spectrum was recorded and the normalized fragmentation yield (Y) was derived, taking into account the 35\% contribution of 13C\textsubscript{12}C\textsubscript{59}\textsuperscript{•+} to the signal (I) at m/z 721:

\[
Y = \frac{L_{720}}{0.65 \left( L_{720} + L_{721} \right)}
\]

The fragment fluence S, which is proportional to the absorption cross-section, is then obtained as

\[
S = -\ln(1 - Y)
\]

S is then plotted as a function of the IR wavelength to provide a surrogate for the ion’s IR spectrum. For every wavelength point, five mass spectra were averaged. S was corrected linearly for wavelength-dependent variations in the laser pulse energy and for the irradiation time (number of applied laser pulses). From repeated scans of the spectrum, we estimate that dissociation yields are reproducible to within about 5\%. The FELIX wavelength is calibrated with a grating spectrometer with an accuracy of ±0.01 \mu m.
Spectra were recorded in the vibrational fingerprint region between 6 μm and 25 μm (ref. 13). The FELIX pulses have an energy of up to 120 mJ and are produced at a 10 Hz repetition rate. Each pulse has a duration of about 7 ps and consists of a series of micropulses spaced by 1 ps. The micropulses are Fourier-transform limited and have a bandwidth of 0.4% of the IR wavelength.

The high dissociation threshold of the protonated fullerene ions makes the application of photodissociation spectroscopy challenging, especially in the long-wavelength range. In order to facilitate the on-resonance IR laser-induced dissociation, the standard helium pressure settings of the ion trap, usually used to efficiently trap the ions, was reduced to its minimum value to minimize collisional deactivation of the ions during IR excitation14. The degree of on-resonance dissociation was controlled by varying the laser pulse energy and by irradiating with a variable number of laser pulses (typically between 2 and 10) to prevent excessive depletion of the C60Hþ precursor ion, which would manifest itself as a saturation at strong absorption bands in the IR spectrum.

Computational investigations of the C60Hþ system were carried out at the DFT level using different combinations of functionals and basis sets. The hybrid B3LYP functional, known for its reliable performance in predicting IR spectra, was used in combination with a series of basis sets of increasing size: 3-21G, 4-31G (which has long been the standard in characterization of IR spectra for large PAHs32,39) and 6-311+G(d,p). In addition, the non-hybrid B3P86 functional (with the 4-31G basis set) was tested, analogous to strategies used in the computation of PAH IR spectra40, as well as the more recent dispersion-corrected functional M06-2X41.

All calculations employed the Gaussian16 software package as installed at the Cartesius supercomputer at SurfSARA, Amsterdam. Geometry optimizations were performed with the standard convergence criteria and vibrational spectra were computed within the harmonic oscillator approximation and harmonic frequencies were scaled uniformly as recommended by ref. 41: 0.9679 for B3LYP/6-311+G(d,p), 0.9525 for B3LYP/4-31G, 0.9583 for B3LYP/3-21G, 1.0033 for BP86/4-31G, 0.9520 for MP2/6-31G(d,p). The computational cost for the geometry optimization and the harmonic frequencies calculation at the B3LYP/6-311+G(d,p) level of theory (2,168 primitive Gaussians) amounts to approximately 10 days on our 16-core computer cluster. For comparison with experiment, the computed stick spectra were convoluted with a Gaussian lineshape function with a full-width at half-maximum (FWHM) of 20 cm−1, which is on the order of bandwidths typically observed in IRMPD spectra and which is believed to be due to a combination of laser bandwidth, rotational envelope and anharmonic broadening and shifting induced by the IRMPD process17.

To estimate the frequency of the single C–H stretch band in C60Hþ, which we were unable to observe experimentally, we used the B3LYP/6-311+G(d,p) harmonic value and an appropriate frequency scaling factor. It is known that the scaling factor for C–H stretch bands typically deviates from that for bands at longer wavelengths18. Therefore, we estimate this factor using B3LYP/6-311+G(d,p) computed spectra for pyrene and phenanthrene and comparing the C–H stretch frequencies with accurate gas-phase IR data19. A scale factor of 0.9610 ± 0.0005 is established, in agreement with ref. 20. This gives a value of 2.850 cm−1 for the C–H stretch mode of C60Hþ.

We note here that the astronomical spectra shown in this paper are emission spectra, resulting from radiative cooling of the species in the ISM after UV excitation and internal conversion15. Despite the fact that the IR emission process leaves its imprint on the appearance of the spectrum, as has been addressed in several studies22, the spectral comparison with simulated spectra is often performed with the help of theoretical calculations with linear vibrational spectra obtained through laboratory transmission spectra or quantum-chemical calculations. A generic redshift of 5–10 cm−1 or a frequency scaling is often applied to empirically correct for the small deviations. The laboratory spectrum of C60Hþ reported here was obtained through IRMPD, which leaves its own imprint on the spectrum, which has been modelled in several studies as well23. Again, deviations from linear vibrational spectra are small enough that spectral analyses are very commonly based on comparisons with linear spectra, as we do here in Fig. 3. The main challenge in correctly modelling IR emission and IRMPD spectra is that this requires parameters for line shifting and broadening as a consequence of anharmonicity, which are typically not available or accessible to determine accurately from quantum-chemical investigations. It is then interesting to note that although the processes of IR multiphoton absorption and IR radiative cooling are different, they are dependent on the same molecular parameters, including these elusive mode-specific anharmonic parameters. To some extent, it may therefore be more appropriate to compare IR emission spectra with IRMPD spectra than with linear IR spectra. In any case, shifts are typically small, as is, for instance, evidenced by the good correspondence between our experimental IRMPD spectrum and the computed (linear) scaled harmonic spectrum of C60Hþ at the B3LYP/6-311+G(d,p) level.

From these considerations, we suggest that the band positions in our experimental spectra can be used directly for C60Hþ. FWHM bandwidths of about 20 cm−1 and slightly smaller at wavelengths near 20 μm are also expected to be close to those in an interstellar emission spectrum. Relative intensities may be less reliable as a consequence of nonlinearities resulting from the IRMPD method; moreover, a correction for the bias towards longer wavelengths in an emission spectrum needs to be taken into account16,17.
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Author contributions

J.P., J.M. and G.B. carried out the experiments, which were conceptualized by J.O. and G.B.; J.P. and J.O. wrote the manuscript with input from all other authors.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials

should be addressed to J.O.

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