

Spectroscopy of helium-tagged C_{60} anions

Miriam Kappe ¹, Paul Martini ², Arne Schiller ^{1,3}, Elisabeth Gruber,¹ Fabio Zappa ¹,
Serge A. Krasnokutski ⁴, Paul Scheier ¹ and Michael Gatchell ^{2,*}

¹*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstrasse 25, A-6020 Innsbruck, Austria*

²*Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden*

³*Institut für Atemgasanalytik, Universität Innsbruck, Innrain 66, A-6020 Innsbruck, Austria*

⁴*Laboratory Astrophysics Group of the Max Planck Institute for Astronomy, Friedrich Schiller University Jena, Helmholtzweg 3, 07743 Jena, Germany*



(Received 30 May 2023; revised 24 January 2024; accepted 2 February 2024; published 1 March 2024)

We present measurements of the electronic absorption spectrum of He-tagged buckminsterfullerene anions, C_{60}^- . Using a technique that allows for the efficient tagging of complex molecular anions with He, we achieve atomically resolved action spectra that provide an accurate determination of the gas-phase absorption spectrum in the near-infrared regime. In total we identify 27 absorption bands between 895 and 1057 nm.

DOI: [10.1103/PhysRevResearch.6.L012045](https://doi.org/10.1103/PhysRevResearch.6.L012045)

The accurate measurement of the gas-phase absorption spectrum of cold C_{60}^+ ions in 2015 [1] was a seismic shift on numerous fronts [2]. It resulted in the first ever definitive identification of a carrier of the so-called diffuse interstellar bands (DIBs), hundreds of ubiquitous absorption bands of astronomical origin in or near the visible range [3,4], the first of which were discovered 100 years ago [5]. The difficulty in identifying DIB carriers is due to a lack of accurate gas-phase absorption spectra for candidate ions and molecules, typically complex carbon-based species. A large molecule such as C_{60} requires temperatures of several hundred degrees Celsius to sublime into the gas phase with high enough densities for direct spectroscopic measurements, limiting the comparability with astronomical observations, and the technical difficulties are even greater for ionic species. Alternatives have been techniques such as matrix isolation spectroscopy, which has been successfully used to measure the absorption spectra of fullerene anions, cations, and neutrals [6,7]. However, this approach comes with its own problems, such as chemical shifts to band positions and line broadening that are difficult to correct for.

The breakthrough measurement of the absorption spectrum of C_{60}^+ was achieved using a method known as messenger spectroscopy [8,9]. The concept of messenger spectroscopy is simple: The ion being studied forms a loosely bound complex with a weakly interacting messenger atom or molecule, which is also known as a tag. When the tagged species absorbs a photon, an internal conversion process excites the system

vibrationally, causing it to dissociate, which can be detected using mass spectrometry. In order to record an absorption spectrum, this measurement is performed as a function of wavelength as a tunable laser is scanned. Compared to conventional spectroscopic techniques that require high column densities of the system being studied, messenger spectroscopy has the advantage of being mass specific and sensitive enough that individual ions can be probed [10]. Nevertheless, the method comes with its own set of challenges. As is the case with matrix isolation measurements, the tags will induce a shift to the absorption bands of an ion. This is typically weaker the weaker is the interaction between the tagged ion and the tags. For this reason, He atoms are generally seen as the ideal tag for messenger spectroscopy [11]. Because of the weak binding energy of He to most ions, He tagging requires cooling the ions down to temperatures of no more than a few Kelvin and can be difficult for large, complex molecular ions. The first measurements of He-tagged C_{60}^+ were performed in a cryogenically cooled ion trap [1,12,13]. There, the trapped fullerene ions were cooled by the introduction of a He buffer gas. As the ions cooled, ions tagged with up to three He atoms were prepared for the spectroscopic measurements. This work was the culmination of two decades of work perfecting this method for use with fullerenes and resulted in the positive identification of five DIBs originating from C_{60}^+ [1,14].

An alternative route for forming He-tagged ions is to start with droplets of superfluid He, an approach that was used to verify the C_{60}^+ spectrum shortly after the first reported results using the trapping technique [15–17]. There, helium nanodroplets (HNDs) with an equilibrium temperature of 0.37 K were doped with fullerene molecules before being ionized by energetic electrons. The ionization process caused charged dopants to be ejected from the droplets, occasionally as loosely bound complexes with He atoms. In this way, He-tagged C_{60}^+ with anywhere from a single to more than 100 He atoms attached could be probed using a tunable laser [15,17].

*gatchell@fysik.su.se

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International license](https://creativecommons.org/licenses/by/4.0/). Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Funded by [Bibsam](https://www.bibsam.org/).

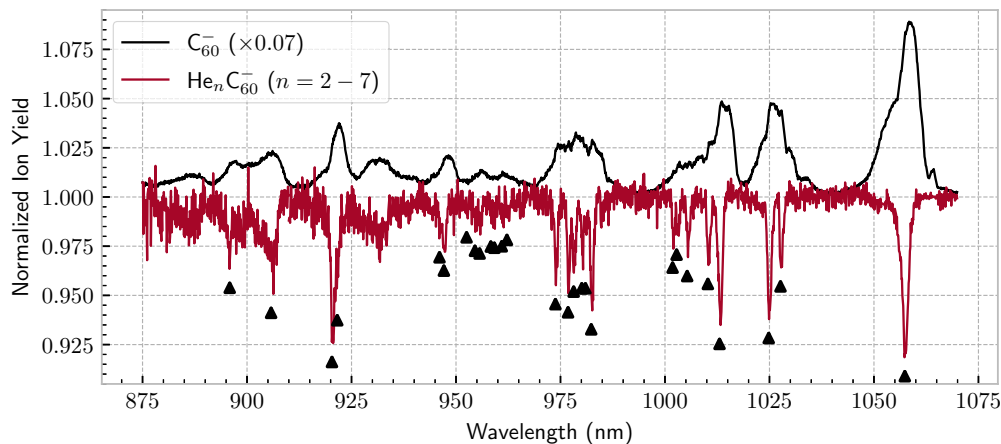


FIG. 1. Overview spectra of He-tagged C_{60}^- anions in the range from 875 to 1075 nm as measured by the increase in yield of bare C_{60}^- ions (black) or the depletion of loosely bound $He_n C_{60}^-$, $n = 2-7$, complexes (red). Band positions and relative yields in the depletion spectrum are indicated by black arrowheads.

The result was an absorption spectrum of C_{60}^+ where the shift induced by the surrounding He atoms could be studied in detail as a function of the number of solvating atoms. Both techniques have since then been successfully used to measure the absorption spectra of other complex molecular ions [18–23], but no additional DIB carriers have yet been identified.

Messenger spectroscopy of He-tagged ions has, however, had a longstanding issue: It is far more challenging to produce He-tagged *anions* than it is cations [24]. This is because the binding energy between anions and solvating He atoms is generally lower than for the equivalent cations. Messenger spectroscopy of anions has been achieved using other tags, for instance, Ar [25] and H_2 [26]. Furthermore, the absorption spectra of anions have been measured for species fully submerged in large HNDs [27], which in essence is a type of matrix isolation spectroscopy. However, literature results of messenger spectroscopy of molecular anions using small numbers of He tags are elusive.

Here, we report on experimental measurements of the electronic absorption spectrum of C_{60}^- ions in the range of 875–1075 nm using the He-tagging technique. This was achieved owing to a recent advancement in the production of cold ions using HNDs. The full details of the setup are given elsewhere [28] and is only briefly described here. Helium nanodroplets were ionized by the impact of 22 eV electrons. This led to a buildup of negatively charged centers in the droplets consisting predominantly of He^{*-} ions [29,30]. The charged droplets then passed through a pickup cell where C_{60} powder was sublimated in an oven. Gas-phase fullerenes that interacted with the droplets were captured and, due to polarization effects, attracted to the charge centers. The fullerenes were subsequently ionized by capturing an electron from He^{*-} while at the same time being cooled to 0.37 K, the equilibrium temperature of the surrounding droplet. The ions were extracted into the gas phase by impacting the droplets onto a stainless steel surface at a right angle. The majority of the ions liberated in this way carry with them loosely bound He atoms, ranging in numbers from a single atom to hundreds, which serve as tags for our spectroscopy measurements. This

method, where the droplets are ionized before pickup and then impacted onto a surface, has proven to increase the yields of He-tagged anions by several orders of magnitude over previous techniques and is key to obtaining high enough yields of tagged anions for spectroscopic measurements [28]. The ions were irradiated by a tunable optical parametric oscillator (OPO) laser (EKSPLO NT-242) with a repetition rate of 1 kHz and the products were analyzed with a reflectron time-of-flight mass spectrometer (Tofwerk AG model HTOF) operating with a 10 kHz duty cycle. Cycles where the laser did not fire were used to correct for variations in the ion beam intensity throughout the measurements.

The measured absorption spectrum for C_{60}^- is shown in Fig. 1. Two curves are shown here, the depletion of $He_n C_{60}^-$ clusters summed over $n = 2-7$ (red) and the increase in yield of bare C_{60}^- (black) as a function of laser wavelength. The depletion curve displays more than two dozen narrow absorption bands starting from the band of the first electronic transition near 1057 nm. The C_{60}^- yield curve has a high signal-to-noise ratio but a poor resolution that is comparable to matrix isolation measurements [6,7]. The reason for this is that the latter measurement probes the products of $He_n C_{60}^-$ clusters photodissociating into bare fullerene ions with no preselection of the number of He tags (n). This spectrum therefore contains a cumulative contribution of all of the band shifts induced by the different numbers of He atoms. Several of the broad features seen in the bare C_{60}^- spectrum have been reported previously [6,7]. In comparison, the mass-selected depletion spectrum shows that these originate from groups of narrow absorption bands. Close-ups of the ion depletion data for $He_2 C_{60}^-$ are given in the Supplemental Material [31].

A close-up of the absorption band pair near 1025 nm is shown in Fig. 2 for different mass-selected $He_n C_{60}^-$ ion complexes. Gaussian absorption profiles have been fitted to the data in this figure and are shown as the black solid lines. Between the different curves we can see a clear shift in the band positions as a function of the number of solvating He atoms. From $n = 2$ to $n = 8$ there is only a slight redshift visible. However, as n increases, the shift in the band positions increases significantly. After $n = 32$, the bands then begin to

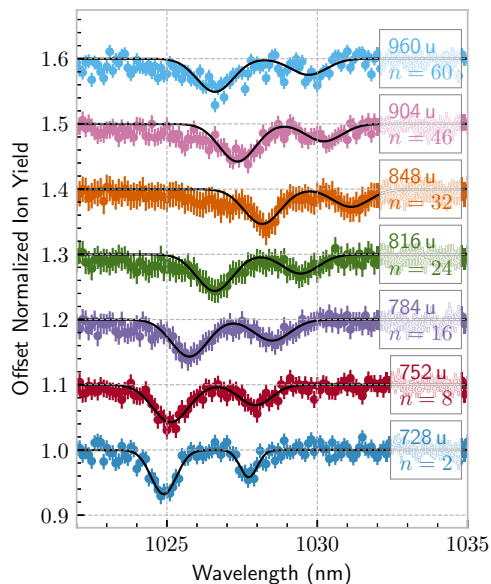


FIG. 2. Positions of He_nC₆₀[−] absorption band pair near 1024.8 nm for different values of n . The bands are redshifted by up to 3 nm with a maximum for $n = 32$.

migrate back towards shorter wavelengths. This overall trend is seen for all of the bands visible in our measured spectra except for the one at 1057 nm. For $n = 2$ to $n = 8$, the 1057-nm band shows a similar behavior to the other bands. But for $n \geq 9$ this band splits into two separate profiles, with a smaller secondary band appearing near 1052 nm (shown more clearly in the Supplemental Material [31]). We attribute this apparent splitting to the presence of residual H₂O molecules in our experimental setup that bind to the C₆₀[−] ions in addition to the He. Since two water molecules have nearly the same mass as nine He atoms, we are unable to separate the contributions of the two different types of complexes with the resolution provided by our mass spectrometer. This extra band is the reason why the 1057-nm band displays a prominent shoulder to the left in the C₆₀[−] yield curve in Fig. 1. A similar, albeit much weaker, splitting is seen in the 963.5-nm band of He-tagged

C₆₀⁺ [17]. There, the splitting was caused by differences in the binding energy of He to the pentagonal and hexagonal faces of C₆₀⁺ between the electronic ground state and the specific excited state involved in the transition. A similar mechanism may explain the observed splitting here, with the larger shift being caused by the stronger interaction between C₆₀[−] and H₂O and the increased polarizability of the anions. The area ratios of the two resulting bands are found to vary around 1.5 for different values of n , which is close to the ratio of hexagons per pentagon (20/12) in the C₆₀[−] structure, lending support for this hypothesis. We do not detect any such influence to the other bands, however, and the residual water has no effect on the spectra of He_nC₆₀[−] ions for $n < 9$ in any case.

The center position of the 1024.8-nm band is shown in Fig. 3 as a function of the number of He tags. In this figure we also show a direct comparison to the band position of the 963.2-nm band for He-tagged C₆₀ cations over the same range and which are in agreement with previous measurements [15]. While the cations show a nearly linearly increasing redshift in the band position for $n \leq 32$, the influence that the He has on the band positions for the anions has a very different appearance. For small n , the band positions are nearly constant, as seen also in Fig. 2. As n increases, the rate with which the band is shifted increases significantly up to $n = 32$. We find that this behavior is well characterized by fitting the functional form

$$\lambda(n) = \lambda_0 + \frac{a}{b-n}, \quad (1)$$

where $\lambda(n)$ is the position of the band center with n solvating He atoms and a and b are free parameters. Since the second half of this expression is nonzero for $n = 0$, the extrapolated gas-phase position of the bands will be given by $\lambda(0) = \lambda_0 + \frac{a}{b}$. The fitted offset of the band centers to this value, $\Delta\lambda(n) = \lambda(n) - \lambda(0)$, is shown as the dashed black curve in Fig. 3. After this, the band center shifts essentially linearly as a function of n towards shorter wavelengths until $n = 60$, after which the band position remains scattered around a constant wavelength.

This basic behavior, which all of the measured bands share, largely mimics that of the He-tagged cations. For those,

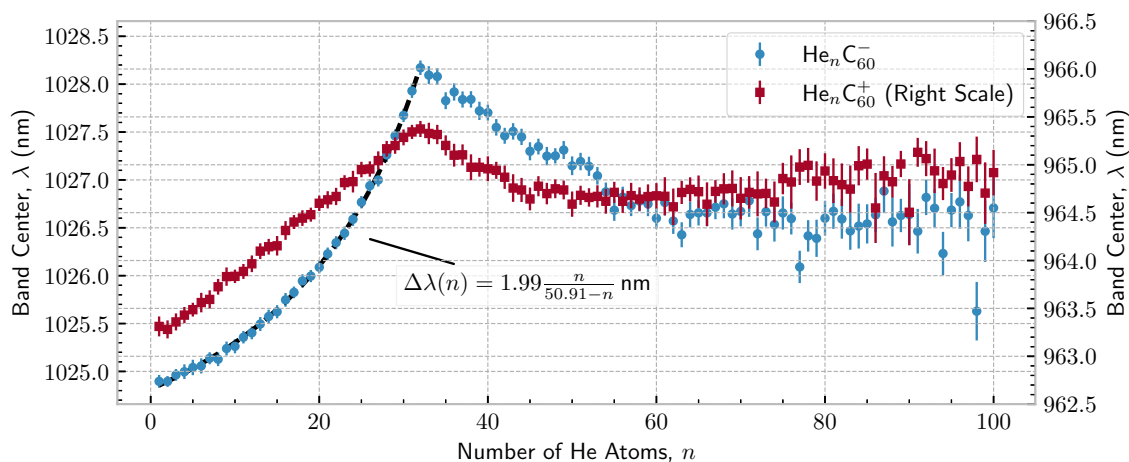


FIG. 3. Center position of the 1024.8-nm absorption band from He_nC₆₀[−] as a function of n (blue, left axis). The position of the 963.2-nm band of He_nC₆₀⁺ is shown for comparison (red, right axis). A hyperbolic fit to the anion data is shown as a dashed black curve.

the maximum redshift at $n = 32$ corresponds to the partial closure of the first solvation layer as the He atoms occupy positions above the 12 pentagonal and 20 hexagonal faces of the fullerene molecules [15,32]. The second process involves fully filling the first solvation layer up to $n = 60$, which perturbs the first sublayer, reducing the average interaction energy of the He atoms with the fullerene ion. After this, additional He layers begin to form which have a significantly weaker interaction with the fullerene than the inner layer. This overall picture of the clustering appears to apply also to $\text{He}_n\text{C}_{60}^-$, a finding that agrees with previous studies [33].

The linear redshift as a function of the number of He atoms surrounding C_{60}^+ (for $n \leq 32$) was explained using a simple model where the fullerene molecule was treated as an isotropically polarizable sphere. This, combined with the observation that the first 32 He atoms formed an essentially solid layer around the fullerene [32], meant that each additional He atom in the first solvation shell redshifted the band positions by an equal amount. This description was clearly reasonable given the good overall agreement between experiment and theory [15]. For the anions, however, this model breaks down. The reason for this is not immediately clear but is likely caused by an anisotropic shift in the electron density resulting from the observed electronic transitions given that the shifts in the band positions are small for the first few attached He atoms. One possible explanation could be that the diffuse orbital of the extra valence electron in C_{60}^- is impeded by the surrounding He layer which reduces the bare surface area available as n increases, giving the observed $1/n$ shift in the band positions. However, this will need to be investigated further before any conclusion can be drawn.

The extracted band positions, relative intensities (σ_{rel}), and widths [full width at half maximum (FWHM) in nm] from Gaussian fits are given in Table I. These were determined from the depletion of the $\text{He}_2\text{C}_{60}^-$ signal and the positions were blueshifted by a constant value of 0.082 nm to give the estimated gas-phase band position. Weaker features, with σ_{rel} less than about 0.05, could not be confidently identified and are not reported. Previous studies indicate that the 1057.5-nm band is the first optically allowed transition ($a_{2u} \rightarrow e_g$) [34] with the bands at shorter wavelengths originating from vibronic states involving the same electronic transition [7]. In addition to the narrow band reported in Table I, there are a few broader features near 880 and 930 nm that were too weak to reliably fit for individual ions depletion signal, but which are apparent in the combined spectra in Fig. 1.

Here, we have demonstrated that He tagging can be used to measure the absorption spectra of cold, complex molecular anions owing to recent developments in experimental techniques with helium nanodroplets. Previous spectroscopic studies of C_{60}^- were carried out using, e.g., matrix isolation spectroscopy at cryogenic conditions [6,7] or of gas-phase ions at elevated temperatures [35,36]. Those measurements provide insight into the electronic and vibrational properties of these ions, but lack the resolution necessary to provide reference spectra for, e.g., astronomical observations. Neutral and cationic fullerenes have been identified in the interstellar

TABLE I. Properties of identified absorption bands.

Band center, air (nm)	(cm^{-1})	σ_{rel}	FWHM (nm)
1057.38(6)	9457.3(0.5)	1.00	1.57
1027.64(7)	9731.1(0.6)	0.23	0.68
1024.81(6)	9757.9(0.6)	0.55	0.99
1013.05(7)	9871.2(0.7)	0.51	1.15
1010.26(7)	9898.5(0.7)	0.22	0.60
1005.31(9)	9947.2(0.8)	0.21	0.75
1002.78(8)	9972.3(0.8)	0.09	0.36
1001.82(10)	9981.8(1.0)	0.14	0.69
982.35(7)	10179.6(0.7)	0.43	0.79
980.97(15)	10194.0(1.5)	0.10	0.69
980.09(8)	10203.1(0.8)	0.11	0.40
978.15(12)	10223.4(1.2)	0.24	1.08
976.81(7)	10237.4(0.7)	0.19	0.50
973.79(8)	10269.2(0.8)	0.29	0.86
962.18(13)	10393.1(1.4)	0.08	0.60
960.94(13)	10406.4(1.4)	0.12	0.87
959.17(7)	10425.6(0.8)	0.11	0.43
958.33(7)	10434.8(0.8)	0.08	0.33
955.65(50)	10464.1(5.5)	0.18	1.49
954.53(32)	10476.4(3.5)	0.07	0.81
952.53(9)	10498.4(1.0)	0.06	0.41
947.10(10)	10558.6(1.1)	0.26	0.90
946.05(12)	10570.3(1.4)	0.13	0.68
921.59(15)	10850.8(1.8)	0.42	1.18
920.32(8)	10865.8(0.9)	0.52	0.74
905.76(11)	11040.5(1.4)	0.61	1.91
895.85(14)	11162.5(1.8)	0.62	2.35

medium (ISM) owing to accurate measurements of electronic and vibrational transition of these species [1,37]. C_{60} anions have been inferred in the ISM from measurements of a 17.51- μm emission band [38,39] but a definitive identification is still elusive. Much work has gone into determining the charge balance of fullerenes in astronomical environments, but accurate measurements of the spectral features of C_{60}^- have hindered the extension of such models to anions [40]. The advancement in He tagging complex molecular anions and the subsequent measurement of the absorption spectrum of C_{60}^- could thus play an important role in expanding our understanding of the chemical composition of the ISM.

This work was supported by the Austrian Science Fund, FWF, Projects No. P31149 and No. I4130, the Swedish Research Council, Projects No. 2016-06625 and No. 2020-03104, and the K-Regio project “FAENOMENAL,” Project No. EFRE 2016-4, funded by the Tyrolian government and the European Regional Development Fund. F.Z. acknowledges support from CNPq. This article is based upon work from COST Actions CA18212–Molecular Dynamics in the GAS phase (MD-GAS) and CA21101–Confined Molecular Systems: From a New Generation of Materials to the Stars (COSY), supported by COST (European Cooperation in Science and Technology).

- [1] E. K. Campbell, M. Holz, D. Gerlich, and J. P. Maier, Laboratory confirmation of C₆₀⁺ as the carrier of two diffuse interstellar bands, *Nature (London)* **523**, 322 (2015).
- [2] H. Linnartz, J. Cami, M. Cordiner, N. L. J. Cox, P. Ehrenfreund, B. Foing, M. Gatchell, and P. Scheier, C₆₀⁺ as a diffuse interstellar band carrier; a spectroscopic story in 6 acts, *J. Mol. Spectrosc.* **367**, 111243 (2020).
- [3] L. M. Hobbs, D. G. York, J. A. Thorburn, T. P. Snow, M. Bishof, S. D. Friedman, B. J. McCall, T. Oka, B. Rachford, P. Sonnentrucker, and D. E. Welty, Studies of the diffuse interstellar bands. III. HD 183143, *Astrophys. J.* **705**, 32 (2009).
- [4] J. Krelowski, Diffuse interstellar bands. A survey of observational facts, *Publ. Astron. Soc. Pac.* **130**, 07100 (2018).
- [5] M. L. Heger, Further study of the sodium lines in class B stars, *Lick Obs. Bull.* **10**, 141 (1922).
- [6] Z. Gasyana, L. Andrews, and P. N. Schatz, Near-infrared absorption spectra of fullerene (C₆₀) radical cations and anions prepared simultaneously in solid argon, *J. Phys. Chem.* **96**, 1525 (1992).
- [7] J. Fulara, M. Jakobi, and J. P. Maier, Electronic and infrared spectra of C₆₀⁺ and C₆₀⁻ in neon and argon matrices, *Chem. Phys. Lett.* **211**, 227 (1993).
- [8] M. Okumura, L. I. Yeh, and Y. T. Lee, The vibrational predissociation spectroscopy of hydrogen cluster ions, *J. Chem. Phys.* **83**, 3705 (1985).
- [9] M. Okumura, L. I. Yeh, J. D. Myers, and Y. T. Lee, Infrared spectra of the solvated hydronium ion: Vibrational predissociation spectroscopy of mass-selected H₃O⁺·(H₂O)_n·(H₂)_m, *J. Phys. Chem.* **94**, 3416 (1990).
- [10] H. J. Zeng, N. Yang, and M. A. Johnson, Introductory lecture: advances in ion spectroscopy: from astrophysics to biology, *Faraday Discuss.* **217**, 8 (2019).
- [11] D. Gerlich, Infrared spectroscopy of cold trapped molecular ions using He-tagging, *J. Chin. Chem. Soc.* **65**, 637 (2018).
- [12] D. Gerlich and S. Horning, Experimental investigation of radiative association processes as related to interstellar chemistry, *Chem. Rev.* **92**, 1509 (1992).
- [13] D. Gerlich, J. Jašík, and J. Roithová, Tagging fullerene ions with helium in a cryogenic quadrupole trap, *Int. J. Mass Spectrom.* **438**, 78 (2019).
- [14] J. P. Maier and E. K. Campbell, The presence of C₆₀⁺ in space, *Int. J. Mass Spectrom.* **434**, 116 (2018).
- [15] M. Kuhn, M. Renzler, J. Postler, S. Ralser, S. Spieler, M. Simpson, H. Linnartz, A. G. G. M. Tielens, J. Cami, A. Mauracher, Y. Wang, M. Alcamí, F. Martín, M. K. Beyer, R. Wester, A. Lindinger, and P. Scheier, Atomically resolved phase transition of fullerene cations solvated in helium droplets, *Nat. Commun.* **7**, 13550 (2016).
- [16] S. Spieler, M. Kuhn, J. Postler, M. Simpson, R. Wester, P. Scheier, W. Ubachs, X. Bacalla, J. Bouwman, and H. Linnartz, C₆₀⁺ and the diffuse interstellar bands: An independent laboratory check, *Astrophys. J.* **846**, 168 (2017).
- [17] A. Kaiser, J. Postler, M. Ončák, M. Kuhn, M. Renzler, S. Spieler, M. Simpson, M. Gatchell, M. K. Beyer, R. Wester, F. A. Gianturco, P. Scheier, F. Calvo, and E. Yurtsever, Isomeric broadening of C₆₀⁺ electronic excitation in helium droplets: Experiments meet theory, *J. Phys. Chem. Lett.* **9**, 1237 (2018).
- [18] F.-X. Hardy, C. A. Rice, and J. P. Maier, Gas-phase electronic spectra of coronene and corannulene cations, *Astrophys. J.* **836**, 37 (2017).
- [19] M. Gatchell, P. Martini, F. Laimer, M. Goulart, F. Calvo, and P. Scheier, Spectroscopy of corannulene cations in helium nanodroplets, *Faraday Discuss.* **217**, 276 (2019).
- [20] M. Meyer, P. Martini, A. Schiller, F. Zappa, S. A. Krasnokutski, and P. Scheier, Electronic Spectroscopy of anthracene cations and protonated anthracene in the search for carriers of diffuse interstellar bands, *Astrophys. J.* **913**, 136 (2021).
- [21] M. Kappe, A. Schiller, S. A. Krasnokutski, M. Ončák, P. Scheier, and E. M. Cunningham, Electronic spectroscopy of cationic adamantane clusters and dehydrogenated adamantane in helium droplets, *Phys. Chem. Chem. Phys.* **24**, 23142 (2022).
- [22] M. Kappe, B. Rasul, M. Mahmoodi-Darian, A. Schiller, F. Zappa, S. A. Krasnokutski, and P. Scheier, He-tagging spectroscopy of tetracene cations, *Mol. Phys.* **122**, e2202271 (2023).
- [23] M. Kappe, A. Schiller, F. Zappa, S. A. Krasnokutski, M. S. Wagner, H. F. Bettinger, and P. Scheier, Electronic spectroscopy of heptacene ions in the search for carriers of diffuse interstellar bands, *Astron. Astrophys.* **672**, A4 (2023).
- [24] J. Simons, M. Johnson, K. Asmis, A. B. McCoy, S. Daly, R. Wester, A. Rijs, P. Sarre, M.-P. Gaigeot, R. Mabbs, K. Jordan, C. Dessent, D. Neumark, C.-w. Chou, B. Gerber, O. Dopfer, J. Oomens, A. Krylov, S. Schlemmer, S. Willitsch *et al.*, Pushing resolution in frequency and time: general discussion, *Faraday Discuss.* **217**, 290 (2019).
- [25] H. K. Gerardi, A. F. DeBlase, X. Su, K. D. Jordan, A. B. McCoy, and M. A. Johnson, Unraveling the anomalous solvatochromic response of the formate ion vibrational spectrum: An infrared, Ar-tagging study of the HCO₂⁻, DCO₂⁻, and HCO₂⁻·H₂O ions, *J. Phys. Chem. Lett.* **2**, 2437 (2011).
- [26] O. Gorlova, J. W. DePalma, C. T. Wolke, A. Brathwaite, T. T. Odbadrakh, K. D. Jordan, A. B. McCoy, and M. A. Johnson, Characterization of the primary hydration shell of the hydroxide ion with H₂ tagging vibrational spectroscopy of the OH⁻·(H₂O)_{n=2,3} and OD⁻·(D₂O)_{n=2,3} clusters, *J. Chem. Phys.* **145**, 134304 (2016).
- [27] D. A. Thomas, E. Mucha, S. Gewinner, W. Schöllkopf, G. Meijer, and G. von Helden, Vibrational spectroscopy of fluoroformate, FCO₂⁻, trapped in helium nanodroplets, *J. Phys. Chem. Lett.* **9**, 2305 (2018).
- [28] P. Martini, S. Albertini, F. Laimer, M. Meyer, M. Gatchell, O. Echt, F. Zappa, and P. Scheier, Splashing of large helium nanodroplets upon surface collisions, *Phys. Rev. Lett.* **127**, 263401 (2021).
- [29] A. Mauracher, M. Daxner, J. Postler, S. E. Huber, S. Denifl, P. Scheier, and J. P. Toennies, Detection of negative charge carriers in superfluid helium droplets: The metastable anions He^{*-} and He₂^{*-}, *J. Phys. Chem. Lett.* **5**, 2444 (2014).
- [30] F. Laimer, F. Zappa, P. Scheier, and M. Gatchell, Multiply charged helium droplet anions, *Chem. Eur. J.* **27**, 7283 (2021).
- [31] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevResearch.6.L012045> for detailed views of measured spectra and the influence of H₂O molecules on the 1057 nm band.
- [32] C. Leidlmair, Y. Wang, P. Bartl, H. Schöbel, S. Denifl, M. Probst, M. Alcamí, F. Martín, H. Zettergren, K. Hansen, O.

- Echt, and P. Scheier, Structures, energetics, and dynamics of helium adsorbed on isolated fullerene ions, *Phys. Rev. Lett.* **108**, 076101 (2012).
- [33] M. Harnisch, N. Weinberger, S. Denifl, P. Scheier, and O. Echt, Adsorption of helium on isolated C_{60} and C_{70} anions, *Mol. Phys.* **113**, 2191 (2015).
- [34] D. R. Lawson, D. L. Feldheim, C. A. Foss, P. K. Dorhout, C. M. Elliott, C. R. Martin, and B. Parkinson, Near-IR absorption Spectra for the buckminsterfullerene anions: an experimental and theoretical study, *J. Electrochem. Soc.* **139**, L68 (1992).
- [35] S. Tomita, J. U. Andersen, E. Bonderup, P. Hvelplund, B. Liu, S. B. Nielsen, U. V. Pedersen, J. Rangama, K. Hansen, and O. Echt, Dynamic Jahn-Teller effects in isolated C_{60}^- studied by near-infrared spectroscopy in a storage ring, *Phys. Rev. Lett.* **94**, 053002 (2005).
- [36] K. Støchkel and J. U. Andersen, Photo excitation and laser detachment of C_{60}^- anions in a storage ring, *J. Chem. Phys.* **139**, 164304 (2013).
- [37] J. Cami, J. Bernard-Salas, E. Peeters, and S. E. Malek, Detection of C_{60} and C_{70} in a young planetary nebula, *Science* **329**, 1180 (2010).
- [38] P. Kupser, J. D. Steill, J. Oomens, G. Meijer, and G. von Helden, IR spectroscopy of gas-phase C_{60}^- , *Phys. Chem. Chem. Phys.* **10**, 6862 (2008).
- [39] S. Iglesias-Groth, Fullerenes in the IC 348 star cluster of the Perseus molecular cloud, *Mon. Not. R. Astron. Soc.* **489**, 1509 (2019).
- [40] G. Rouillé, S. A. Krasnokutski, and Y. Carpentier, The $C_{60}:C_{60}^+$ ratio in diffuse and translucent interstellar clouds, *Astron. Astrophys.* **656**, A100 (2021).