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Letter

Measuring Electronic Transitions Using Leak-Out Spectroscopy

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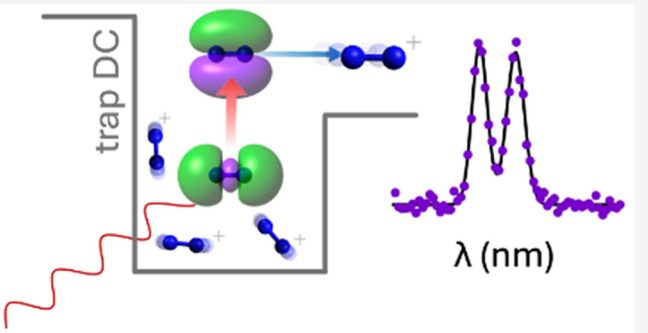
ABSTRACT: We demonstrate that leak-out spectroscopy (LOS) can be employed to measure electronic transitions in the visible and infrared range by recording the electronic spectra of nitrogen, diacetylene, and triacetylene cations. LOS promises to be a general single-photon method for measuring gas phase electronic spectra of mass selected bare ions. LOS is especially promising as a potential method for measuring the electronic spectra of bare ions that are highly photostable, which is an important characteristic of interstellar molecules. Therefore, LOS may be a valuable method for searching for the diffuse interstellar bands.



It is desirable to have a method for measuring the electronic spectra of gas-phase ions that (1) follows the absorption of a single photon, (2) measures an unshifted spectrum of the bare ion, and (3) is applicable for all ions in general. A promising candidate for achieving these goals is leak-out spectroscopy (LOS), which was recently developed by Schmid et al.;[1] however, this has not yet been applied to electronic spectra in the NIR, visible, or UV ranges. Modern strategies for measuring electronic spectra of gas-phase ions employ action spectroscopic techniques, which involve measuring the "action" of an ion after photoexcitation (such as photodissociation, reactions, or fluorescence) as a function of laser frequency. However, each action spectroscopic method has disadvantages or compromises inherent in its deployment. Single-photon resonance enhanced photodissociation spectroscopy is often lifetime broadened;[2] one-color multiphoton dissociation produces broad peaks that are slightly distorted;[3] spectra measured using He nanodroplets or messenger tagging are not spectra of the bare ion;[4] laser-induced reactions,[5] laser-induced inhibition of complex growth,[6] or multiple-color spectroscopy[7,8] typically require sophisticated understanding of the underlying reaction scheme, spectroscopic levels, or subtle experimental conditions to implement. Above the single-photon dissociation threshold, single-photon dissociation spectroscopy is normally sufficiently effective. Therefore, this study focuses on electronic transitions that lie below the single-photon dissociation threshold. Below the single-photon dissociation threshold, one-color multiphoton dissociation can yield distorted peak intensities and shapes because of power broadening or because one cannot generally control whether the subsequent photon absorptions are resonant or nonresonant.[8,9] This is why groups employ two-color multiphoton dissociation techniques to measure precise band positions and widths that are required for astrophysical comparison.[7,8,10−12] Additionally, many ions are too reactive to be straightforwardly investigated in jets, discharges, and absorption cells. Nevertheless, there have been successful studies using cavity ringdown absorption spectroscopy for stable ions in discharges,[8,11,13−15] and for mass-selected ions in ion traps,[16−18] although these techniques are typically much less sensitive than action spectroscopy.[18] Recent work has shown that LOS (which is a type of action spectroscopy) is a sensitive method that does not suffer from the disadvantages of other action spectroscopy methods when measuring rovibrational spectra.[1,19,20] However, the applicability of LOS to the visible and NIR spectral ranges has not been tested yet.

The mechanism underlying electronic LOS is summarized in Figure 1 for N_2^+. Further details are given in the Experimental Section. To measure an electronic LOS spectrum, ions are stored in a cryogenic ion trap with a potential barrier set at the exit electrode such that the ions are only barely trapped. The ions are then irradiated using visible or NIR light from a tunable light source. Photoexcited ions then collide with a neutral buffer gas, causing them to convert part of their elevated internal energy into kinetic energy. This additional kinetic energy enables the ions to overcome the low exit barrier of the ion trap and leak out to the detector.

Following photoexcitation of the ion, there are multiple possible scenarios that can occur *prior* to collision with the neutral gas. (*I*) The ion undergoes radiative decay—such as

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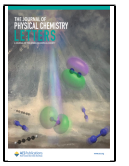

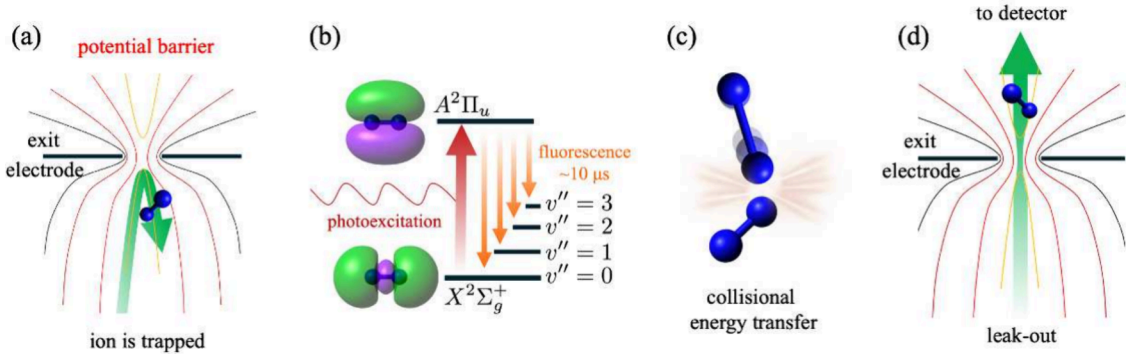

Figure 1. Illustration of a LOS mechanism for an electronic transition of N_2^+. Neutral N_2 was used as a collision partner in (c).

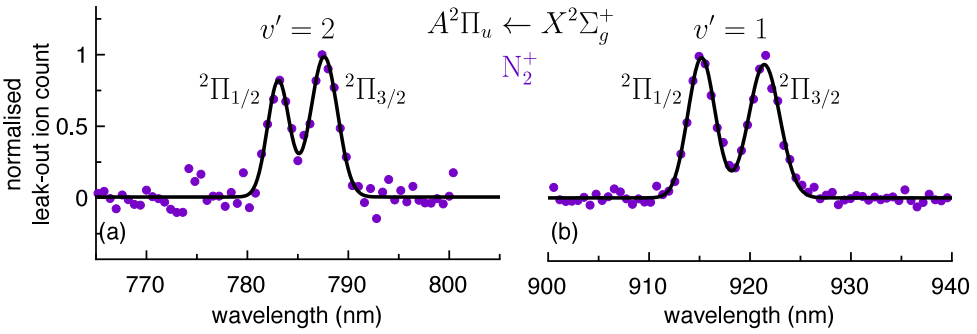

Figure 2. Electronic spectra of N_2^+ measured using leak-out spectroscopy. Leak-out ion signal of m/z 28 is plotted as a function of light wavelength (purple circles). The spectra are fit with Gaussian functions to estimate the bandwidth ($\Delta\lambda \approx 3$ nm), which is determined by the light source.

fluorescence or phosphorescence—which may populate excited vibrational states in the ground electronic state. (*II*) The ion undergoes nonradiative decay—such as internal conversion or intersystem crossing—which populates a lower lying electronic state that is highly vibrationally excited. (*III*) The ion collides with the neutral buffer gas while still in the excited electronic state. (*IV*) The ion can dissociate if it is excited above the dissociation threshold. We neglect photodissociation here, because the transitions of interest to this study are all well below the dissociation threshold. Because of the success of vibrational LOS,[1,20] it can be expected that vibrationally excited ions generated following photoexcitation in scenarios *I* and *II* will yield sufficient vibrational-to-kinetic energy transfer to facilitate leak out. However, this has not yet been demonstrated. Whether electronic-to-kinetic energy transfer can also facilitate leak out (scenario *III*) is another interesting question.

An astrophysical motivation for developing such a method for electronic spectroscopy of gas-phase ions is the search for diffuse interstellar bands (DIBs). DIBs are interstellar absorptions in the visible and NIR range.[21] There are currently hundreds of DIBs reported by astronomers, but only five of them have been attributed to any carrier (C_{60}^+).[22] Various methods that are typically employed to measure spectra of DIB candidates—along with their advantages and disadvantages—have been recently summarized by Douglas-Walker et al., who highlighted the potential of LOS to be a valuable method.[8]

Considering the fact that the vast majority of DIBs remain unidentified, it is important to develop methods that can quickly screen DIB carrier candidates, as highlighted by Roithová et al.[23] This is because confirmation of DIB carriers requires accurate high-resolution spectra (up to $\Delta\bar{\nu} = 0.01$ cm^{-1} for narrow DIBs), but searching the entire visible range ($25000\ cm^{-1}$ to $14000\ cm^{-1}$) with such high resolution for each candidate molecule is impractical.[21,22] Furthermore, calculations are much less accurate for electronic transitions than for rotational or vibrational transitions, which means that experimental methods that can screen candidate molecules are desirable.[24] Previous examples of experimental strategies for screening DIB carrier candidates include matrix isolation spectroscopy,[25] rare gas tagging,[23] and photodissociation with lower resolution light sources ($>1\ cm^{-1}$).[7,26] Electronic LOS provides valuable alternative strategies for quickly screening DIB carrier candidates, as discussed below.

Electronic LOS is also a promising method for assessing candidate molecular ions for potential laser-cooling applications,[27] which need to be photostable and should have resolved rovibronic spectra that can be challenging to precisely measure with traditional ion spectroscopy techniques. There are only very few molecular ions that are known to be good candidates for this because the spectra of many photostable diatomic and triatomic ions remain unknown.

In this Letter, we report proof of concept results that illustrate the effectiveness of LOS to measure electronic transitions of gas phase ions. We measure the spectra of N_2^+, HC_4H^+, and HC_6H^+. These are the first electronic spectra reported in the visible and NIR range using LOS and illustrate the applicability of LOS for measuring one-color electronic spectra of bare ions.

Figure 2 shows electronic transitions of N_2^+ measured using LOS. The light source was a continuous wave white light fiber laser (SuperK FIANIUM) with wavelength tunability controlled by a band-pass filter (LLTF Contrast). The electronic spectra of N_2^+ have been measured by several other methods, including absorption spectroscopy,[28] laser-induced reactions,[5] laser-induced inhibition of complex growth,[6] and laser-induced

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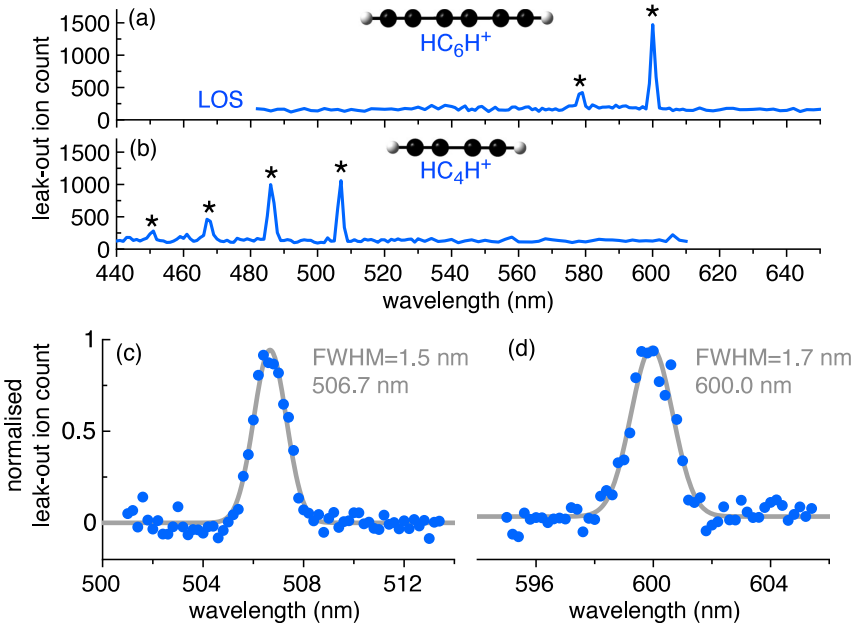

Figure 3. Electronic spectra of (a) HC_6H^+ and (b) HC_4H^+ cations measured using LOS. Asterisks mark the known band positions reported previously.[10−12,15,25,32−35] The origin transitions of (c) HC_4H^+ and (d) HC_6H^+ have been fit to Gaussian functions (gray trace) to estimate the accuracy of their position and width, which are limited by the light source.

fluorescence.[29] The bands in Figure 2 correspond to the $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ electronic transition of N_2^+. The transitions originate from the ground X vibrational state ($v'' = 0$) and excite the ($v' = 1$) or ($v' = 2$) vibrational levels in the upper A state. Spin−orbit coupling between the unpaired electron spin $S = \pm 1/2$ and the orbital angular momentum $\Lambda = 1$ in the $A^2\Pi_u$ state splits the levels in this state into $\Omega = |\Lambda + S| = 1/2$ or $3/2$ components, with the $\Omega = 3/2$ component lower in energy.[30] Considering the broadness of the light source, the spectra of N_2^+ are in complete agreement with previous studies.[5,6,28,31]

Figure 3shows the vibronic spectra of diacetylene (HC_4H^+) and triacetylene (HC_6H^+) cations measured using LOS. These transitions have been measured before by many methods including absorption in neon matrices,[25] two-color photodissociation,[10−12] messenger tagging,[32,33] laser-induced fluorescence,[34] frequency modulation absorption spectroscopy,[35] and cavity ringdown spectroscopy.[11,15] The asterisks in Figure 3 indicate the known positions of the most intense vibronic transitions. The HC_4H^+ electronic transition has $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ character, while the HC_6H^+ electronic transition has $\tilde{A}^2\Pi_g \leftarrow \tilde{X}^2\Pi_u$ character. The most intense transitions are the origin transitions at 507 nm (HC_4H^+) and 600 nm (HC_6H^+). These transitions are then followed by progressions of the lowest frequency σ stretching modes (ν_3 for HC_4H^+ and ν_4 for HC_6H^+), with some contributions from weaker vibronic transitions that we do not resolve with our low resolution light source. The relative intensities of these vibronic transitions are in good agreement with the most realistic relative intensities measured by absorption of cations deposited in neon matrices.[25] Considering the broadness of the light source, the spectra of HC_4H^+ and HC_6H^+ are in complete agreement with previous studies.[10−12,15,25,32−35]

The average time between collisions of N_2^+ ions and neutral N_2 buffer gas was on the order of 1 ms. The N_2^+ cation has a fluorescence lifetime on the order of 10 μs in the $A^2\Pi_u^+$ state,[36] which populates excited vibrational levels in the $X^2\Sigma_g$ state with a quantum yield of >0.5.[5] This means that collisions will mostly occur between vibrationally excited $N_2^+(X^2\Sigma_g)$ ions and the neutral N_2 buffer gas, with some collisions also occurring between electronically excited $N_2^+(A^2\Pi_u^+)$ ions and the neutral N_2 buffer gas. Whether the electronic LOS spectrum arises mostly from electronic to kinetic energy transfer or vibrational to kinetic energy is an interesting question that we do not resolve here. Future studies could investigate this by increasing the collision rate to increase the probability that collisions occur while the ions are still in the excited electronic state or decreasing the collision rate to decrease the probability that collisions occur while the ions are still in the excited electronic state. Another possibility is investigation of electronic spectra for atomic ions like C^+, which obviously cannot vibrate. Whether an electronic to translation (ET) energy transfer is less favorable than the known VT transfer is an open question, but we believe that the ET coupling is weaker than the VT coupling, which is already small compared to the rotation-translation (RT) or elastic energy transfer between the collision partners. Considering the success of vibrational LOS, it seems clear that vibrationally excited ions generated by electronic excitation followed by fluorescence will be able to effectively undergo vibrational to kinetic energy transfer and leak out of the trap.

The fluorescence lifetimes of HC_4H^+ and HC_6H^+ ($\tau_F \approx 10-100$ ns)[37] are much lower than that of N_2^+ and approximately 10^5 times faster than the collision rate. Therefore, these ions are much more likely to undergo photoexcitation and fluorescence and then vibrational to kinetic energy transfer, allowing the ions to leak out. These results support the effectiveness of leak out following fluorescence to excited ground state vibrational levels. This is encouraging because it suggests that electronic excited states of ions that are efficiently deactivated by photon emission can be interrogated using LOS.

The nonradiative decay of the $\tilde{A}$ state of HC_4H^+ is an order of magnitude slower than the radiative rate.[38] This means that

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radiative decay occurs significantly more than nonradiative decay for HC_4H^+. For larger molecules, nonradiative decay is generally more prevalent because of their larger density of states. Nonradiative decay can quickly convert electronically excited ions into the ground electronic state with a high internal vibrational energy. This situation is probably favorable for electronic leak-out spectroscopy, as it would result in higher internal vibrational energies for ions relative to radiative decay. This is consistent with our observation that the electronic LOS spectrum of HC_6H^+ was easier to measure than that of HC_4H^+, and HC_6H^+ appears to undergo nonradiative decay with larger quantum yield based on its similar oscillator strength (f = 0.06) to HC_4H^+ (f = 0.04) and its shorter $\tilde{A}$ state lifetime (τ = 17 ns) than HC_4H^+ (τ = 71 ns).[12,37,39] One might expect that the HC_6H^+ electronic LOS spectrum would be harder to measure than that of HC_4H^+ because HC_6H^+ ions were generated with significantly lower ion counts, have a less favorable mass ratio with the neutral N_2 buffer gas, have lower excitation energy, and have a higher likelihood to fluoresce into the ground vibrational state (based on its origin dominated spectrum). Ultimately, our results for HC_6H^+ give a preliminary indication that electronic LOS can effectively occur following nonradiative decay to a vibrationally excited ground electronic state.

Electronic leak-out spectroscopy also enables new strategies for searching for ions with strong electronic transitions. This can be applied to searches for DIBs. With LOS, the trap can simultaneously be filled with many different ions (with different m/z ratios), and the leak-out ion count can be measured while a laser is scanned over known DIB frequencies. As the laser is scanned, the leak-out signal can be measured for any of these ions selectively or all of these ions at once. This would allow simultaneous assessment of many DIB candidates that are formed abundantly from whichever ion source is employed. Furthermore, this method would preferentially identify strong electronic transitions of photostable ions, which are desirable characteristics for DIB candidates.

This strategy is reminiscent of previous studies that scanned over DIB frequencies using cavity ringdown spectroscopy of many molecules formed in discharges and plasmas.[13,14] One example of such a study identified an absorption feature that matched a DIB at 5450 Å, but the identity of the carrier was not determined—other than the fact that it was a hydrocarbon radical or ion.[14] Further investigation assigned this laboratory feature to the H_2CCC radical and argued that H_2CCC is also a DIB carrier.[40] Eventually, this assignment was rejected.[41] A recent study reported another coincidence with this 5450 Å DIB, the cavity ringdown band and an absorption of $HC_{11}H^+$;[26] however, this cannot be the carrier of the laboratory cavity ringdown spectroscopy band observed in ref 14 because of their differing isotopic shifts. These studies illustrate that the strategy of searching for DIB coincidences in complex mixtures of molecules and ions can be effective but identifying the carrier of these laboratory bands is challenging. Undertaking a similar strategy with LOS has the advantage that the m/z of the ion responsible for the absorption feature can be straightforwardly determined. Furthermore, the carrier could also be rigorously investigated with the established vibrational LOS method or other ion spectroscopic techniques to precisely determine its structure. This is promising because it would combine the effectiveness of previous studies for finding DIB coincidences with superior capabilities to identify the carrier.

A proof of concept experiment is shown in Figure 4, which shows a leak-out mass spectrum measured with light on resonance (orange trace) and off resonance (blue trace) with the origin transition of HC_4H^+. Further details about this experiment can be found in the Experimental Section. When irradiated by light on resonance with the HC_4H^+ transition, the leak-out ion count of the HC_4H^+ ion (m/z 50) is greatly enhanced. Experiments like this could be undertaken by setting (or scanning) a laser over the frequency of a DIB to search for a response.

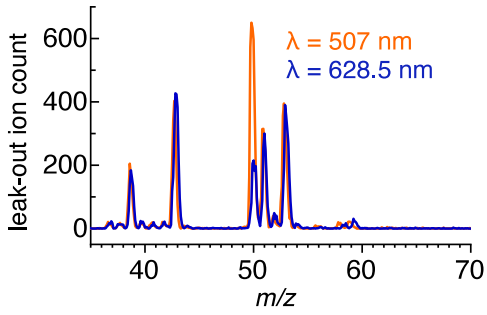

Figure 4. Leak out mass spectra showing the ion count leaking out of the trap as a function of m/z when irradiated with λ = 507 nm light (orange trace, on resonant with HC_4H^+) or λ = 628.5 nm light (blue trace, off resonant with HC_4H^+).

In summary, we have demonstrated that LOS is effective for measuring electronic transitions of gas-phase ions in the visible and NIR wavelength ranges using the case studies of N_2^+, HC_4H^+, and HC_6H^+. Our results indicate that electronic leak out can effectively occur following fluorescence from an upper electronic state to vibrationally excited levels of the ground state or by nonradiative decay to vibrationally hot low lying electronic states. The width and signal of the measured transitions are currently limited by the broad light source and can be improved by employing higher resolution and higher power lasers. Electronic LOS is a particularly promising method for searching for carriers of DIBs because it can effectively measure the single photon spectra of photostable bare ions. One downside of LOS is that it requires sufficient energy transfer into the kinetic energy, which will be less efficient for larger ions. Because C_{60}^+ is the only known DIB carrier, we note that spectra of large ions such as C_{60}^+ should be more challenging to measure using LOS. The LOS setup employed in this work is limited by the quadrupole mass filters mass cutoff; however, future work will target larger ions and test these mass constraints. Furthermore, we note that leak-out spectroscopy could be a good method for finding candidates for small molecular ions that can be laser cooled by using their electronic transitions, which also require single photon spectra of photostable bare ions.

EXPERIMENTAL SECTION

Spectra were measured using leak-out spectroscopy (LOS) in the cryogenically cooled 22-pole ion trap apparatus referred to as LIRtrap.[5,42] This method has been described in detail previously for vibrational spectroscopy.[1] For N_2^+, ions were formed from N_2 gas, which was ionized in a storage ion source by 70 eV electrons. The ions were pulsed out of the source every 5 s into a quadrupole mass filter (QMF1), which selected m/z 28. The mass selected ions exiting the QMF1 were then trapped and stored in a 22-pole ion trap mounted on a 10 K

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cold-head.[43] The ion trap in this study was heated to 44 K to avoid freeze out of neutral N_2 buffer gas that was allowed into the trap region with a continuous number density of approximately 10^{12} cm^{-3}. As the ions enter the trap, they are intersected with a pulse of neutral He gas from a *piezo* valve that decelerated and cooled the ions. Light from a continuous white light fiber laser (SuperK FIANIUM) was filtered by a high resolution band-pass filter (LLTF Contrast), and the tunable output (10 mW/cm^2) was used to irradiate the ions for 4.95 s, the timing of which was controlled by a mechanical shutter. The output light has a relatively broad bandwidth (*fwhm* = 1−3 nm), which makes the effective power quite low for narrow transitions. Nevertheless, this light source is suitable for overview spectra. Excited ions could collide with neutral N_2 gas to transfer their excess internal energy into kinetic energy. The ions with enhanced kinetic energy could overcome the low potential barrier at the trap exit and leak out of the trap. After exiting the trap, ions passed through a second quadrupole mass filter (QMF2) set to select m/z 28, before being detected using a Daly type detector.[44,45] This process was repeated while the light frequency was scanned to record a LOS spectrum. The baseline counts drifted over the course of the experiment due to partial freeze out of the background N_2 gas, which was corrected for in Figures 2, 3c and 3d by fitting the background ion counts to a third order polynomial and subtracting it from the raw ion counts. Experiments using HC_4H^+ and HC_6H^+ were also undertaken employing essentially the same workflow as that for N_2^+, only with different quadrupole settings to select their m/z values and with acetylene gas in the storage ion source. The total trapped ion counts were on the order of 10^5 ions for N_2^+ and HC_4H^+, and 10^4 ions for HC_6H^+.

To measure a leak-out mass spectrum (Figure 4), QMF1 was set to RF only mode to allow a wide range of m/z values to enter the trap. The trap exit barrier was set so that approximately 1% of the ions m/z leaked out after the 5 s trapping time. The m/z selection of the QMF2 was then scanned and the leak out ion count of each m/z value was recorded.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.5c01674.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Schmid, P. C.; Asvany, O.; Salomon, T.; Thorwirth, S.; Schlemmer, S. Leak-out spectroscopy, a universal method of action spectroscopy in cold ion traps. *J. Phys. Chem. A* **2022**, *126*, 8111−8117.

(2) Pino, G. A.; Feraud, G.; Broquier, M.; Grégoire, G.; Soorkia, S.; Dedonder, C.; Jouvet, C. Non-radiative processes in protonated diazines, pyrimidine bases and an aromatic azine. *Phys. Chem. Chem. Phys.* **2016**, *18*, 20126−20134.

(3) Bomse, D.; Woodin, R.; Beauchamp, J. Molecular activation with low-intensity CW infrared laser radiation. Multiphoton dissociation of ions derived from diethyl ether. *J. Am. Chem. Soc.* **1979**, *101*, 5503−5512.

(4) Salomon, T.; Brackertz, S.; Asvany, O.; Savić, I.; Gerlich, D.; Harding, M. E.; Lipparini, F.; Gauss, J.; van der Avoird, A.; Schlemmer, S. The He−H_3^+ complex. II. Infrared predissociation spectrum and energy term diagram. *J. Chem. Phys.* **2022**, *156*, 144308.

(5) Schlemmer, S.; Kuhn, T.; Lescop, E.; Gerlich, D. Laser excited N_2^+ in a 22-pole ion trap:: Experimental studies of rotational relaxation processes. *Int. J. Mass Spectrom.* **1999**, *185*, 589−602.

(6) Chakrabarty, S.; Holz, M.; Campbell, E. K.; Banerjee, A.; Gerlich, D.; Maier, J. P. A novel method to measure electronic spectra of cold molecular ions. *J. Phys. Chem. Lett.* **2013**, *4*, 4051−4054.

(7) Marlton, S. J.; Buntine, J. T.; Watkins, P.; Liu, C.; Jacovella, U.; Carrascosa, E.; Bull, J. N.; Bieske, E. J. Probing colossal carbon rings. *J. Phys. Chem. A* **2023**, *127*, 1168−1178.

(8) Douglas-Walker, T. E.; Campbell, E. K.; Daly, F. C.; Douin, S.; Gans, B.; Jacovella, U.; Maurice, C.; Odant, R.; Palotás, J. Ion spectroscopy in the context of the diffuse interstellar bands: a case study with the phenylacetylene cation. *ACS Earth Space Chem.* **2024**, *8*, 2644−2651.

(9) Zhao, Y.; de Beer, E.; Xu, C.; Taylor, T.; Neumark, D. M. Spectroscopy and electron detachment dynamics of C_4^-, C_6^-, and C_8^-. *J. Chem. Phys.* **1996**, *105*, 4905−4919.

(10) Chakrabarty, S.; Rice, C.; Mazzotti, F.; Dietsche, R.; Maier, J. Electronic absorption spectrum of triacetylene cation for astronomical considerations. *J. Phys. Chem. A* **2013**, *117*, 9574−9577.

(11) Maier, J.; Chakrabarty, S.; Mazzotti, F.; Rice, C.; Dietsche, R.; Walker, G.; Bohlender, D. Assignment of 5069 Å diffuse interstellar band to HC_4H^+: disagreement with laboratory absorption band. *Astrophys. J. Lett.* **2011**, *729*, L20.

(12) Dzhonson, A.; Jochnowitz, E. B.; Maier, J. P. Electronic gas-phase spectra of larger polyacetylene cations. *J. Phys. Chem. A* **2007**, *111*, 1887−1890.

(13) Ball, C.; McCarthy, M.; Thaddeus, P. Laboratory Detection of a Molecular Band at λ4429. *Astrophys. J.* **2000**, *529*, L61.

(14) Linnartz, H.; Wehres, N.; Van Winckel, H.; Walker, G.; Bohlender, D.; Tielens, A.; Motylewski, T.; Maier, J. A coincidence between a hydrocarbon plasma absorption spectrum and the λ5450 DIB. *Astron. Astrophys.* **2010**, *511*, L3.
(15) Motylewski, T.; Linnartz, H.; Vaizert, O.; Maier, J.; Galazutdinov, G.; Musaev, F.; Krełowski, J.; Walker, G.; Bohlender, D. Gas-phase electronic spectra of carbon-chain radicals compared with diffuse interstellar band observations. *Astrophys. J.* **2000**, *531*, 312.
(16) Terasaki, A.; Majima, T.; Kondow, T. Photon-trap spectroscopy of mass-selected ions in an ion trap: optical absorption and magneto-optical effects. *J. Chem. Phys.* **2007**, *127*, 231101−231101.
(17) Chu, W.; Yu, C.; Xiao, Z.; Zhang, Q.; Chen, Y.; Zhao, D. Gas-phase optical absorption spectra of the indene cation ($C_9H_8^+$). *Mol. Phys.* **2023**, *121*, No. e2150703.
(18) Egashira, K.; Terasaki, A. Optical absorption spectrum of the chromium dimer cation: Measurements by photon-trap and photodissociation spectroscopy. *Chem. Phys. Lett.* **2015**, *635*, 13−15.
(19) Salomon, T.; Baddeliyanage, C.; Schladt, C.; Simko', I.; Császár, A. G.; Silva, W. G.; Schlemmer, S.; Asvany, O. High-resolution leak-out spectroscopy of HHe_2^+. *Phys. Chem. Chem. Phys.* **2025**, *27*, 4826−4828.
(20) Steenbakkers, K.; van Boxtel, T.; Groenenboom, G. C.; Asvany, O.; Redlich, B.; Schlemmer, S.; Brünken, S. Leak-out spectroscopy as alternative method to rare-gas tagging for the Renner−Teller perturbed $HCCH^+$ and $DCCD^+$ ions. *Phys. Chem. Chem. Phys.* **2024**, *26*, 2692−2703.
(21) Hobbs, L. M.; York, D. G.; Snow, T. P.; Oka, T.; Thorburn, J. A.; Bishof, M.; Friedman, S. D.; McCall, B.; Rachford, B.; Sonnentrucker, P.; Welty, D. E. A catalog of diffuse interstellar bands in the spectrum of HD 204827. *Astrophys. J.* **2008**, *680*, 1256.
(22) Campbell, E. K.; Holz, M.; Gerlich, D.; Maier, J. P. Laboratory confirmation of C_{60}^+ as the carrier of two diffuse interstellar bands. *Nature* **2015**, *523*, 322−323.
(23) Roithová, J.; Jašík, J.; Mellado, J. J. D. P.; Gerlich, D. Electronic spectra of ions of astrochemical interest: from fast overview spectra to high resolution. *Faraday Discuss.* **2019**, *217*, 98−113.
(24) Loos, P.-F.; Scemama, A.; Jacquemin, D. The quest for highly accurate excitation energies: A computational perspective. *J. Phys. Chem. Lett.* **2020**, *11*, 2374−2383.
(25) Fulara, J.; Grutter, M.; Maier, J. P. Higher excited electronic transitions of polyacetylene cations $HC_{2n}H^+$ n = 2−7 in neon matrixes. *J. Phys. Chem. A* **2007**, *111*, 11831−11836.
(26) Marlton, S. J.; Liu, C.; Watkins, P.; Bieske, E. J. Gas-phase electronic spectra of $HC_{2n+1}H^+$ (n= 2−6) chains. *Phys. Chem. Chem. Phys.* **2024**, *26*, 12306−12315.
(27) Nötzold, M.; Wild, R.; Lochmann, C.; Wester, R. Spectroscopy and ion thermometry of C_2^- using laser-cooling transitions. *Phys. Rev. A* **2022**, *106*, 023111.
(28) Benesch, W.; Rivers, D.; Moore, J. High resolution spectrum of the N_2^+ Meinel system to 11 250 Å. *J. Opt. Soc. Am.* **1980**, *70*, 792−799.
(29) Niikura, H.; Mizutani, M.; Mitsuke, K. Rotational state distribution of N_2^+ produced from N_2 or N_2O observed by a laser−synchrotron radiation combination technique. *Chem. Phys. Lett.* **2000**, *317*, 45−52.
(30) Ventura, L. R.; da Silva, R. S.; Amorim, J.; Fellows, C. E. A new look at N_2^+electronic transitions: An experimental and theoretical study. *J. Mol. Spectroscop.* **2024**, *401*, 111902.
(31) Jusko, P.; Jiménez-Redondo, M.; Caselli, P. Cold CAS ion trap−22 pole trap with ring electrodes for astrochemistry. *Mol. Phys.* **2024**, *122*, No. e2217744.
(32) Muller, G.; Catani, K. J.; Scholz, M. S.; Jacovella, U.; Bartlett, N. I.; Bieske, E. J. Electronic spectra of diacetylene cations (HC_4H^+) tagged with Ar and N_2. *J. Phys. Chem. A* **2019**, *123*, 7228−7236.
(33) Jacovella, U.; Muller, G.; Catani, K. J.; Bartlett, N. I.; Bieske, E. J. Electronic Spectra of the Triacetylene Cation (HC_6H^+) and Protonated Triacetylene ($HC_6H_2^+$) Tagged with Ar. *Aus. J. Chem.* **2019**, *72*, 260−266.
(34) Lecoultre, J.; Maier, J. P.; Rösslein, M. Geometric structure of diacetylene cation in the $X^2\Pi_g$ and $A^2\Pi_u$ electronic states. *J. Chem. Phys.* **1988**, *89*, 6081−6085.
(35) Pfluger, D.; Sinclair, W. E.; Linnartz, H.; Maier, J. P. Rotationally resolved electronic absorption spectra of triacetylene cation in a supersonic jet. *Chem. Phys. Lett.* **1999**, *313*, 171−178.
(36) Lofthus, A.; Krupenie, P. H. The spectrum of molecular nitrogen. *J. Phys. Chem. Ref. Data* **1977**, *6*, 113−307.
(37) Allan, M.; Kloster-Jensen, E.; Maier, J. P. Emission spectra of the radical cations of diacetylene ($A^2\Pi_u \rightarrow X^2\Pi_g$), triacetylene ($A^2\Pi_g \rightarrow X^2\Pi_u$), and tetraacetylene ($A^2\Pi_u \rightarrow X^2\Pi_g$), and the lifetimes of some vibronic levels of the $\tilde{A}$ states. *Chem. Phys.* **1976**, *17*, 11−18.
(38) Maier, J. P.; Thommen, F. Radiative and nonradiative decay rates of state selected $H-(C\equiv C)_2-H^+$, $D-(C\equiv C)_2-D^+$, $\tilde{A}^2\Pi_\omega$ determined by a photoelectron−photon coincidence technique. *J. Chem. Phys.* **1980**, *73*, 5616−5619.
(39) Freivogel, P.; Fulara, J.; Lessen, D.; Forney, D.; Maier, J. P. Absorption spectra of conjugated hydrocarbon cation chains in neon matrices. *Chem. Phys.* **1994**, *189*, 335−341.
(40) Maier, J.; Walker, G.; Bohlender, D.; Mazzotti, F.; Raghunandan, R.; Fulara, J.; Garkusha, I.; Nagy, A. Identification of H_2CCC as a diffuse interstellar band carrier. *Astrophys. J.* **2011**, *726*, 41.
(41) Krełowski, J.; Galazutdinov, G.; Kołos, R. Can H_2CCC be the carrier of broad diffuse bands? *Astrophys. J.* **2011**, *735*, 124.
(42) Schlemmer, S.; Lescop, E.; von Richthofen, J.; Gerlich, D.; Smith, M. A. Laser induced reactions in a 22-pole ion trap: $C_2H_2^+ + h\nu + H2 \rightarrow C_2H_3^+ + H$. *J. Chem. Phys.* **2002**, *117*, 2068−2075.
(43) Asvany, O.; Bielau, F.; Moratschke, D.; Krause, J.; Schlemmer, S. Note: New design of a cryogenic linear radio frequency multipole trap. *Rev. Sci. Instrum.* **2010**, *81*, 076102.
(44) Daly, N. Scintillation type mass spectrometer ion detector. *Rev. Sci. Instrum.* **1960**, *31*, 264−267.
(45) Asvany, O.; Brünken, S.; Kluge, L.; Schlemmer, S. COLTRAP: a 22-pole ion trapping machine for spectroscopy at 4 K. *Appl. Phys. B: Laser Opt.* **2014**, *114*, 203−211.

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