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Formation of astrochemically relevant molecular ions: reaction of translationally cold CCl^+ with benzene in a linear ion trap

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The gas-phase ion-neutral reaction of CCl^+ + benzene (C_6H_6) is investigated using a linear Paul ion trap coupled to a time-of-flight mass spectrometer. Low collision energies are achieved by sympathetically cooling CCl^+ reactant ions with co-trapped laser-cooled Ca^+. The observed products include the astrochemically relevant carbocations ${C_7H_5}^+$, ${C_5H_3}^+$, and ${C_3H_3}^+$, as well as $C_3H_2Cl^+$. Branching ratios of these products are measured and ${C_7H_5}^+$, a carbon-growth species, is favored. Complementary electronic structure calculations provide thermodynamic limits for the reaction and allow for assignment of reaction products to specific structural isomers. Only one exoergic isomer is identified for each observed product, with the exception of ${C_7H_5}^+$, where many identified structural isomers are exoergic. The results from this work broaden our understanding of the reactivity and possible role of CCl^+ and C_6H_6 in interstellar chemistry. Furthermore, this study provides insight into a potential pathway to larger carbocations that may be precursors to more complex polycyclic aromatic hydrocarbons.

Rich chemistry takes place in regions that we still know relatively little about, such as areas of the interstellar medium (ISM) and planetary atmospheres. This chemistry is slowly being understood through a multidisciplinary effort focused on laboratory and theoretical studies, as well as physical measurements from new space exploration missions.[1–13] Within this larger effort, ion-neutral reactions have been identified as requiring more experimental exploration, especially at lower temperatures.[4] This is because ion-neutral reactions are known to have much faster rates than neutral-neutral reactions, and thus, are predicted to have a more prominent role in the chemistry present in these remote areas.[4, 14] Of particular interest are the ion-neutral reaction pathways that lead to carbon molecular weight growth and perhaps to polycyclic aromatic hydrocarbons (PAHs). Interest in PAHs is fueled by their ubiquity in, and importance to, the chemistry of many regions of the ISM.[5, 15–21] Interest has also been due to speculation that PAHs could be the carriers for the diffuse interstellar bands (DIBs), the mostly unidentified absorption features seen towards reddened stars and other extraterrestrial objects.[5, 13] Only ${C_{60}}^+$ has been confirmed as a carrier, but the PAH hypothesis has fueled many spectroscopic and kinetic studies of potential PAH carriers and formation reactions.[5, 10, 13]. The spectroscopy of several PAHs has been well understood, but it remains to be demonstrated exactly how they form. A promising pathway involves additions of small ions to small aromatics (including benzene).[1, 4–7, 12, 14] Much work remains to investigate reactions within this category before a clear picture of this process can emerge. This requires exploration of candidate reactions to define their dynamics and potential role in such a process. Controlled, low temperature and pressure terrestrial kinetics and dynamics experiments can reproduce the conditions of the remote areas of the ISM and beyond, providing a clearer understanding of the complex reaction pathways and mechanisms in these environments.

Here, we report on the ion-neutral reaction of CCl^+ + C_6H_6, measured for the first time in a low temperature and pressure regime. C_6H_6 has been identified in the atmosphere of Jupiter, Saturn, and Titan (one of Saturn's moons)[2, 3, 8, 9] and has been tentatively identified in interstellar and circumstellar environments using mid-infrared spectroscopy.[22, 23] Benzenes participation in ISM chemistry is established, including reactivity with highly abundant atomic species such as H, O, C and N+.[1, 24–29] So far, CCl^+ has not been considered a primary player in interstellar chlorine chemistry because its abundance is uncertain and was thought to be primarily inert to many (but not all) interstellar species.[30–34] Only recently has the reactivity of CCl^+ been illuminated through experimental efforts by our group. Specifically, its reactivity has been demonstrated with astrochemically relevant molecules acetylene and acetonitrile at low collision energies[35, 36]. These studies support the hypothesis that CCl^+ has a hitherto underrepresented role in the chemistry that is occurring in the ISM. Potential abundances and plausible locations of CCl^+ are inferred with the aid of measured reactions and rate constants, as well as predictions and models of chemistry involving CCl^+. Thus, we believe CCl^+ to be an important molecule to study, even preceding a definite conclusion regarding its abundance in the ISM.The main ionic products from the reaction presented here include ${C_7H_5}^+$, ${C_3H_3}^+$, ${C_5H_3}^+$, and $C_3H_2Cl^+$, of which ${C_3H_3}^+$ has been identified and the rest have been speculated to exist in various areas in the ISM and beyond.[2, 37–40] Importantly, the reaction results in a carbon growth pathway that could be consequential to chemistry in the ISM, planetary atmospheres, and other remote areas.

The exploration of cold and controlled reactions is a vibrant and growing field.[41–44] Our experimental ap-

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paratus shown in Fig. 1 allows for the exploration of ion-neutral interactions under cold conditions.[45–49] The setup is comprised of a linear Paul ion trap coupled to a time-of-flight mass spectrometer (LIT-TOFMS). While the ultra-high vacuum environment of the apparatus is denser than the sparsest regions of space, it mimics the single-collision conditions of space, in which three-body reactions are extremely unlikely. This apparatus also allows for controlled reactions between translationally cold, trapped ions and neutral reactant gas over long interrogation times. Low collision energies (here 8 meV or ∼93 K) are achieved by direct laser cooling of Ca^+, which sympathetically cools the translational motion of the co-trapped CCl^+ reactant ions. The cold conditions combined with the TOF-MS provide excellent mass resolution enabling clear chemical formula assignments from the resulting mass spectra. The significant energetic constraints on the reaction and identified chemical formulas enable more facile comparison to calculations at the CCSD(T)/CBS//CCSD/aug-cc-pVDZ level of theory, allowing for accurate determination of the thermodynamic limits of the reaction (within 0.04 eV). While temperature conditions in the ISM vary widely (from a few Kelvin to millions of Kelvin), we aim to understand reactions in the coldest conditions that we can achieve. This combination of experimental and computational tools allows for a clearer view of the chemistry of the important, and yet unexplored, reaction of $CCl^+ + C_6H_6$ under conditions comparable to various remote areas of space.

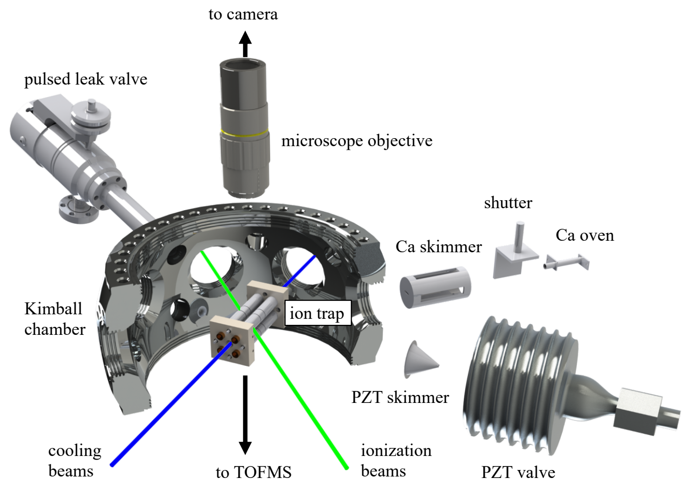

FIG. 1. Schematic diagram of the LIT-TOFMS used for measuring the reaction of $CCl^+ + C_6H_6$. CCl^+ ions are produced by non-resonant photoionizaton and sympathetically cooled by the co-trapped laser-cooled Ca^+. Approximately 2×10^{-10} Torr neutral C_6H_6 (11% in Helium, 300 K) is leaked into the vacuum chamber via a pulsed leak valve scheme for a set duration (0, 10, 90, 170, 240, or 320 s). After each reaction step, the resulting ions are then ejected into the TOF-MS, giving highly resolved mass spectra for each time step. Reproduced with permission from Schmid et *al.*, Phys. Chem. Chem. Phys. 22, 20303 (2020). Copyright 2020 The Royal Society of Chemistry.

Kinetic data for the reaction of $CCl^+ + C_6H_6$ are shown in Fig. 2. As the reaction progressed, the majority of the trapped CCl^+ reacted away into four products: ${C_3H_3}^+$ (m/z 39), ${C_5H_3}^+$ (m/z 63), $C_3H_2Cl^+$ (m/z 73), and ${C_7H_5}^+$ (m/z 89). These observed products were used to construct a reaction model in order to fit the reaction data and extract reaction rates and product branching ratios (see Tab. I). Under our experimental conditions, C_6H_6 is in excess, allowing for the use of a pseudo-first-order kinetic model, which includes a set of differential equations (given in SI) used to fit the experimentally observed ion numbers as a function of time (resulting fits shown as solid lines in Fig. 2). Notably, in this reaction, the majority of CCl^+ reacted away, although in the time frame of our experiments some remained. This timescale was chosen mainly because the principal focus of the study was to determine the primary products and their branching fractions, as opposed to measuring subsequent reactions of the primary products with benzene. The products shown here can be identified as primary products by the profile of the number of ions measured as a function of time. These product ions have the largest growth rate when the CCl^+ numbers are at their greatest, and continue to grow while the CCl^+ is in the trap. This holds true for data taken at early time points, as shown in the Supplemental Information. Additionally, secondary ion products are not detected in the trap and the total number of ions (summed over products and reactants) does not change over the course of a reaction, which implies that all ion products are detected. (Data showing the conservation of ion number during a reaction can be found in the SI.)

Kinetic data for the reaction of $C^{37}Cl^+ + C_6H_6$ was also measured (see SI for reaction curves), and this reaction was used as a mechanism for the identification of chlorinated products in order to refine molecular formula assignments. Indeed, only one observed mass product changed when the heavier $C^{37}Cl^+$ was used, $m/z\,73 \to 75$, confirming its assignment as $C_3H_2Cl^+$. Overall, we can be certain that the products were comprised only of the atoms in the reactants (that is, C, H or Cl), because we begin our reactions with a clean sample of either CCl^+ or $C^{37}Cl^+$ (see methods section in the SI for details). Product assignments are further supported by computational modeling discussed below. Although it is not the focus of the current study, it should be noted that the rate of reaction for $C^{37}Cl^+$ is twice as fast as that for CCl^+, indicating that a kinetic isotope effect may be at play here, driving the faster rate.

Branching ratios for each of the observed products were obtained by dividing the separate product growth rates by the CCl^+ loss rate (see Tab. I). Branching of the $CCl^+ + C_6H_6$ reaction favored the ${C_7H_5}^+$ product by about 50% compared to the other observed products. Additionally, we confirmed conservation of trapped ions

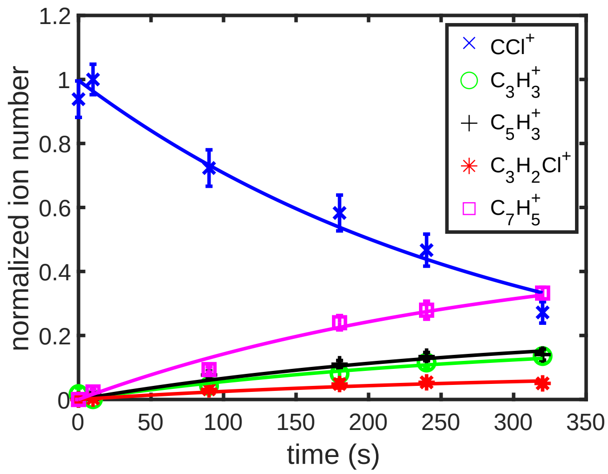

FIG. 2. Rate reaction data (points) and fits (curves) for pseudo-first-order reaction of $CCl^+ + C_6H_6$. CCl^+ (blue ×) reacts with excess C_6H_6 resulting in first-order products $C_3H_3{}^+$ (green ○), $C_5H_3{}^+$ (black +), $C_3H_2Cl^+$ (red ∗), and $C_7H_5{}^+$ (magenta □).

TABLE I. Branching ratios for the primary products of CCl^+ and $C^{37}Cl^+$ reacting with C_6H_6. The numbers are given as percentages and uncertainties are derived from the 90% confidence interval from the pseudo-first-order model fits.

Reactants	$C_3H_3{}^+$	$C_5H_3{}^+$	$C_3H_2Cl^+$	$C_7H_5{}^+$
$CCl^+ + C_6H_6$	19(2)	23(2)	9(1)	49(4)
$C^{37}Cl^+ + C_6H_6$	24(2)	18(1)	11(1)	46(4)

by monitoring the total ion number as a function of trap time. These data were collected for the reactions of CCl^+ and $C^{37}Cl^+$ with C_6H_6 and are provided in the SI.

The lowest energy structural isomers for each product channel are plotted in Fig. 3, with additional isomers for each channel given in the SI. The product isomers presented for each observed mass in Fig. 3 are significantly more exoergic relative to the reactants at the CCSD(T)/CBS//CCSD/aug-cc-pVDZ level of theory and may all be formed. It is assumed that a reaction complex forms as the reaction proceeds, particularly because the $C_3H_2Cl^+$ and $C_7H_5{}^+$ products have constituents of both reactants. From such a reaction complex, various steps may be required before fragmentation into the experimentally observed products. Ideally, a potential energy surface would be used to connect the reactants and products and would yield a more rigorous comparison to experimental branching ratios. This would be a large undertaking. Even without a calculated potential energy surface, we are able to demonstrate which isomers contribute to observed experimental products. This is because of the tight energetic constraints of our cold experimental conditions (∼93 K, 8 meV). This assumes a room temperature ro-vibrational distribution of the reactants and products. Although we conducted an exhaustive computational search for all possible isomers of each mass channel and corresponding neutral, some higher energy isomers may not have been found.

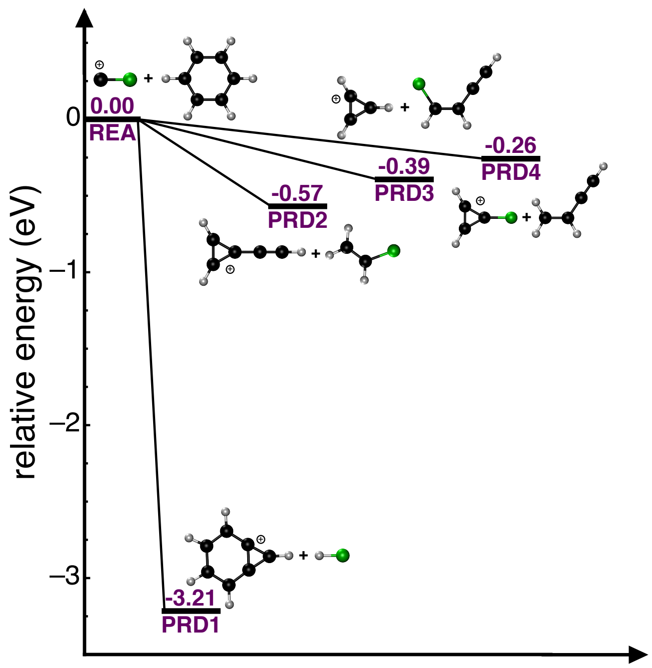

FIG. 3. Energetic limits for the reaction of $CCl^+ + C_6H_6$ going to four different products, $C_7H_5{}^+$ + HCl, $C_5H_3{}^+$ + C_2H_3Cl, $C_3H_2Cl^+$ + C_4H_4 and $C_3H_3{}^+$ + C_4H_3Cl. All products are exoergic with respect to the reactants at the CCSD(T)/CBS//CCSD/aug-cc-pVDZ level of theory. The bare '+' denotes infinite distance between the ion-neutral pair and the inscribed '+' symbol corresponds to the ion of the ion-neutral pair.

Only one ion-neutral pair was found to be exoergic for the $C_3H_2Cl^+ + C_4H_4$ and $C_5H_3{}^+ + C_2H_3Cl$ products shown as PRD4 and PRD2 respectively in Fig. 3. Because these ions are energetically favorable and the other closest available isomers are > 200 meV higher in energy, it should be straightforward to assign the m/z 73 product to the PRD4 isomer of $C_3H_2Cl^+$ and the m/z 63 product to the PRD2 isomer of $C_5H_3{}^+$. For $C_3H_3{}^+$ + C_4H_3Cl, the lowest energy pair for this product is shown as PRD3 in Fig. 3. The only energetically favorable ion for this channel is the cyclopropenyl cation (c-$C_3H_3{}^+$) shown in Fig. 3, which we assign to the m/z 39 product. The assignment of m/z 39 to c-$C_3H_3{}^+$ is consistent with the observed ions not continuing to react with C_6H_6 in the experiment. The reaction of c-$C_3H_3{}^+$ with C_6H_6 is known to be very slow compared to the linear propargyl isomer, further supporting this assignment.[14] A few neutral C_4H_3Cl isomers are energetically favorable for this channel. However, because the neutral is not trapped in our experiments, it is not possible to know its exact identity.

In contrast to the other products, there are several possible exoergic isomers that could be assigned to the HCl loss product, $C_7H_5{}^+$. The lowest energy isomer, shown in Fig. 3 as PRD1, is much more exoergic than any of the other possible products. The increased number of viable isomers, and the exoergicity of the products, might give insight into why this channel is experimentally favored. There may be submerged barriers to some of the energetically favorable isomers of $C_7H_5{}^+$ that would complicate this simplistic interpretation. Thus, a full potential energy surface and kinetic modeling of this reaction would be enlightening and could be of broad interest to the question of PAH production. We hope that others will continue with these efforts.

There are no experiments with which we can directly compare our results and predicted products. Similar products have been seen before for reactions of $C^+ + C_6H_6$, using ion cyclotron resonance mass spectrometry and a crossed molecular beam apparatus over collision energies of 0.02-12 eV.[14, 50–53] However, because of the difference in ionization energies between the two reactants, the main product measured was $C_6H_6{}^+$ and constituted a branching of 67-85%. The $C_7H_5{}^+$ product was observed, but with only a modest branching of up to 10%.[53] This is in contrast to our observation of $CCl^+ + C_6H_6$, where $C_7H_5{}^+$ constitutes 50% of the products. The shared carbon growth product between the two reactions is intriguing and even more so that branching to $C_7H_5{}^+$ in the reaction with CCl^+ is more heavily favored. Of course, it is likely that the differences in these reactions are at least partially attributed to the presence of the chlorine atom. The high electronegativity of chlorine likely impacts the distribution of electron density in the reaction complex, in which case, the energy landscape of the reaction dramatically changes. Further computational work and reaction studies of this type, including with other halogenated carbocations and C_6H_6, may illuminate a possible mechanism for this carbon growth.

The experimentally favored HCl loss channel product, $C_7H_5{}^+$, must be formed by the addition of the carbon atom from CCl^+ to the ring of C_6H_6. This reaction could provide another mechanism for growth of carbonaceous species and possibly PAH formation in low temperature and pressure environments. As discussed above, because so many of the possible $C_7H_5{}^+$ isomers are exoergic with respect to the reactants, it is difficult to pinpoint which $C_7H_5{}^+$ isomer is formed in this reaction. However, this represents an intriguing step to uncovering a possible new pathway to larger carbonaceous species, which might be consequential to chemistry taking place in the ISM, planetary atmospheres, or other environments. Hopefully, this work will inspire further experimental and theoretical studies towards understanding additional pathways to complex organic molecules and carbon molecular weight growth.

From this and other reaction studies, CCl^+ itself has a growing basis for consideration as an astrochemically relevant molecule. While a positive identification in the ISM is yet to be made, its potential to participate in interstellar chemistry via reactions with other interstellar molecules has been demonstrated[35, 36, 54]. In fact, a high-resolution rotational spectrum of CCl^+ has recently been measured by Asvany *et al.*[55] and it can be expected that the question of whether it exists in the ISM be answered in the near future.

This work has outlined the reaction of CCl^+ with C_6H_6 and shows a new pathway to multiple astrochemically relevant carbocations, $C_3H_3{}^+$, $C_5H_3{}^+$, and $C_7H_5{}^+$, as well as $C_3H_2Cl^+$. With the aid of computational work, only one possible exoergic product for each channel was identified, except in the case of $C_7H_5{}^+$, in which several viable exoergic isomers exist. The reactants and products each comprise definite or possible participants in ISM chemistry, and the formation of the favored product, $C_7H_5{}^+$, may illuminate a new pathway to molecular weight growth of carbonaceous species. This could have possible implications for the creation of complex organic molecules and perhaps PAHs in the ISM, planetary atmospheres, and other extraterrestrial environments. The complex chemistry connecting smaller carbocations to larger PAHs is still being understood and more reaction studies with various molecules are required to fully understand the progression from small carbocations to complex molecules like $C_{60}{}^+$. We believe this reaction contributes to this important open question, and presents a very intriguing first step to carbon growth at colder temperatures from CCl^+ reacting with the abundant C_6H_6.

I. ACKNOWLEDGEMENTS

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II. SUPPLEMENTAL INFORMATION

See supplementary information for expanded experimental results, including the reaction curve for $C^{37}Cl^+ + C_6H_6$, details of reaction curve fits, and for more detailed computational results. In addition, more details regarding the experimental and theoretical methods can be found there, which includes citations [56–72].

III. REFERENCES

[1] Theodore P Snow, Valery Le Page, Yeghis Keheyan, and Veronica M Bierbaum. The interstellar chemistry of PAH cations. *Nature*, 391(6664):259–260, 1998.

[2] J. H. Waite, D. T. Young, T. E. Cravens, A. J. Coates, F. J. Crary, B. Magee, and J. Westlake. The process of tholin formation in titan's upper atmosphere. *Science*, 316(5826):870–875, 2007.

[3] V. Vuitton, R. V. Yelle, and J. Cui. Formation and distribution of benzene on titan. *J. Geophys. Res. Planets*, 113(E5), 2008.

[4] Theodore P Snow and Veronica M Bierbaum. Ion Chemistry in the Interstellar Medium. *Annual Rev. Anal. Chem.*, 1(1):229–259, 2008.

[5] A.G.G.M. Tielens. Interstellar polycyclic aromatic hydrocarbon molecules. *Annu. Rev. Astron. Astrophys.*, 46(1):289–337, 2008.

[6] Eric Herbst and Ewine F. van Dishoeck. Complex organic interstellar molecules. *Annu. Rev. Astron. Astrophys.*, 47(1):427–480, 2009.

[7] A. G. G. M. Tielens. The molecular universe. *Rev. Mod. Phys.*, 85:1021–1081, 2013.

[8] J. H. Westlake, J. H. Waite Jr., N. Carrasco, M. Richard, and T. Cravens. The role of ion-molecule reactions in the growth of heavy ions in titan's ionosphere. *J. Geophys. Res. Space Physics*, 119:5951–5963, 2014.

[9] Bruno Bézard, Pierre Drossart, Thérèse Encrenaz, and Helmut Feuchtgruber. Benzene on the giant planets. *Icarus*, 154(2):492–500, 2001.

[10] E K Campbell, M Holz, D Gerlich, and J P Maier. Laboratory confirmation of ${C_{60}}^+$ as the carrier of two diffuse interstellar bands. *Nature*, 523(7560):322–323, 2015.

[11] Christian P Endres, Stephan Schlemmer, Peter Schilke, Jürgen Stutzki, and Holger SP Müller. The cologne database for molecular spectroscopy, cdms, in the virtual atomic and molecular data centre, vamdc. *J. Mol. Spectrosc.*, 327:95–104, 2016.

[12] Eric Herbst. The synthesis of large interstellar molecules. *Int. Rev. Phys. Chem.*, 36:287–331, 2017.

[13] E. K. Campbell. Spectroscopy of astrophysically relevant ions in traps. *Mol. Phys.*, 118:1–12, 2020.

[14] Diethard K. Bohme. Pah and fullerene ions and ion/molecule reactions in interstellar and circumstellar chemistry. *Chem. Rev.*, 92:1487–1508, 1992.

[15] D. Calzetti, R. C. Kennicutt, C. W. Engelbracht, C. Leitherer, B. T. Draine, L. Kewley, J. Moustakas, M. Sosey, D. A. Dale, K. D. Gordon, G. X. Helou, D. J. Hollenbach, L. Armus, G. Bendo, C. Bot, B. Buckalew, T. Jarrett, A. Li, M. Meyer, E. J. Murphy, M. Prescott, M. W. Regan, G. H. Rieke, H. Roussel, K. Sheth, J. D. T. Smith, M. D. Thornley, and F. Walter. The calibration of mid-infrared star formation rate indicators. *Astrophys. J.*, 666(2):870–895, sep 2007.

[16] J. D. T. Smith, B. T. Draine, D. A. Dale, J. Moustakas, Jr. R. C. Kennicutt, G. Helou, L. Armus, H. Roussel, K. Sheth, G. J. Bendo, B. A. Buckalew, D. Calzetti, C. W. Engelbracht, K. D. Gordon, D. J. Hollenbach, A. Li, S. Malhotra, E. J. Murphy, and F. Walter. The mid-infrared spectrum of star-forming galaxies: Global properties of polycyclic aromatic hydrocarbon emission. *Astrophys. J.*, 656(2):770–791, feb 2007.

[17] Jacqueline Kessler-Silacci, Jean-Charles Augereau, Cornelis P. Dullemond, Vincent Geers, Fred Lahuis, Neal J. Evans II, Ewine F. van Dishoeck, Geoffrey A. Blake, A. C. Adwin Boogert, Joanna Brown, Jes K. Jorgensen, Claudia Knez, and Klaus M. Pontoppidan. C2d spitzer irs spectra of disks around t tauri stars. i. silicate emission and grain growth. *Astrophys. J.*, 639(1):275–291, Mar 2006.

[18] L. Verstraete, J. L. Puget, E. Falgarone, S. Drapatz, C. M. Wright, and R. Timmermann. SWS spectroscopy of small grain features across the M17-Southwest photodissociation front. *Astron. Astrophys.*, 315:L337–L340, November 1996.

[19] A. Omont. Physics and chemistry of interstellar polycyclic aromatic molecules. *Astron. Astrophys.*, 164:159–178, August 1986.

[20] A. Leger and J. L. Puget. Identification of the "unidentified" IR emission features of interstellar dust? *Astron. Astrophys.*, 500:279–282, 1984.

[21] J. L. Puget and A. Leger. A new component of the interstellar matter: small grains and large aromatic molecules. *Annu. Rev. Astron. Astrophys.*, 27:161–198, 1989.

[22] José Cernicharo, Ana M. Heras, A. G. G. M. Tielens, Juan R. Pardo, Fabrice Herpin, Michel Guélin, and L. B. F. M. Waters. Infrared space observatory's discovery of C_4H_2, C_6H_2, and benzene in CRL 618. *Astrophys. J.*, 546(2):L123–L126, 2001.

[23] J. Bernard-Salas, E. Peeters, G. C. Sloan, J. Cami, S. Guiles, and J. R. Houck. The spitzer IRS spectrum of SMP LMC 11. *Astrophys. J.*, 652(1):L29–L32, 2006.

[24] Simon Petrie, Gholamreza Javahery, and Diethard K. Bohme. Gas-phase reactions of benzenoid hydrocarbon ions with hydrogen atoms and molecules: uncommon constraints to reactivity. *J. Am. Chem. Soc.*, 114(23):9205–9206, 1992.

[25] Graham B. I. Scott, David A. Fairley, Colin G. Freeman, Murray J. McEwan, Nigel G. Adams, and Lucia M. Babcock. $CmHn^+$ reactions with h and H_2: An experimental study. *J. Phys. Chem. A*, 101(27):4973–4978, 1997.

[26] Serge A. Krasnokutski and Friedrich Huisken. Ultra-low-temperature reactions of c(3p0) atoms with benzene molecules in helium droplets. *J. Chem. Phys.*, 141(21):214306, 2014.

[27] Steven J. Sibener, Richard J. Buss, Piergiorgio Casavecchia, Tomohiko Hirooka, and Yuan T. Lee. A crossed molecular beams investigation of the reactions o(3p)+ c6h6, c6d6. *The Journal of Chemical Physics*, 72(8):4341–4349, 1980.

[28] AJ Colussi, DL Singleton, RS Irwin, and RJ Cvetanovic. Absolute rates of oxygen (3p) atom reactions with benzene and toluene. *The Journal of Physical Chemistry*, 79(18):1900–1903, 1975.

[29] D. Ascenzi, P. Franceschi, T.G.M. Freegarde, P. Tosi, and D. Bassi. Cn bond formation in the reaction of nitrogen ions n+ with benzene molecules. *Chemical Physics Letters*, 346(1):35–40, 2001.

[30] David A. Neufeld and Mark G. Wolfire. The chemistry of interstellar molecules containing the halogen elements. *Astrophys. J.*, 706(2):1594–1604, nov 2009.

[31] Kinsuk Acharyya and Eric Herbst. Gas-grain fluorine and chlorine chemistry in the interstellar medium. *Astrophys. J.*, 850:105, 2017.

[32] J. Glosik, D. Smith, P. Španěl, W. Freysinger, and W. Lindinger. SIFDT studies of the reactions of C^+, CH^+ and ${CH_2}^+$ with HCl and CO_2, and ${CH_3}^+$ with HCl. *Int. J. Mass Spectrom. Ion Processes*, 129(C):131–143, 1993.

[33] D. Smith and N. G. Adams. Production and loss processes for HCl in interstellar clouds: some relevant laboratory measurements. *Astrophys. J.*, 298:827–829, 1985.

[34] G. A. Blake, V. G. Anicich, and Jr. Huntress, W. T. Chemistry of Chlorine in Dense Interstellar Clouds. *As-*

trophys. J., 300:415, January 1986.
[35] K. J. Catani, J. Greenberg, B. V. Saarel, and H. J. Lewandowski. Reactions of translationally cold trapped CCl^+ with acetylene (C_2H_2). *J. Chem. Phys.*, 152(23):234310, 2020.
[36] O. A. Krohn, K. J. Catani, J. Greenberg, S. P. Sundar, G. da Silva, and H. J. Lewandowski. Isotope-specific reactions of acetonitrile (CH_3CN) with trapped, translationally cold CCl^+. *J. Chem. Phys.*, 154:074305, 2021.
[37] A. Ali, E.C. Sittler, D. Chornay, B.R. Rowe, and C. Puzzarini. Cyclopropenyl cation – the simplest huckel's aromatic molecule – and its cyclic methyl derivatives in titan's upper atmosphere. *Planetary and Space Science*, 87:96 – 105, 2013.
[38] Vincent G. Anicich, Daniel B. Milligan, David A. Fairley, and Murray J. McEwan. Termolecular Ion–Molecule Reactions in Titan's Atmosphere, I: Principal Ions with Principal Neutrals. *Icarus*, 146(1):118 – 124, 2000.
[39] A Korth, M L Marconi, D A Mendis, F R Krueger, A K Richter, R P Lin, D L Mitchell, K A Anderson, C W Carlson, H Rème, J A Sauvaud, and C D'Uston. Probable detection of organic-dust-borne aromatic ${C_3H_3}^+$ ions in the coma of comet Halley. *Nature*, 337(6202):53–55, 1989.
[40] D. Smith. The ion chemistry of interstellar clouds. *Chem. Rev.*, 92(7):1473–1485, 1992.
[41] Prateek Puri, Michael Mills, Ionel Simbotin, John A Montgomery, Robin Côté, Christian Schneider, Arthur G Suits, and Eric R Hudson. Reaction blockading in a reaction between an excited atom and a charged molecule at low collision energy. *Nature Chemistry*, 11(7):615–621, 2019.
[42] Tiangang Yang, Anyang Li, Gary K. Chen, Qian Yao, Arthur G. Suits, Hua Guo, Eric R. Hudson, and Wesley C. Campbell. Isomer-specific kinetics of the C^+ + H_2O reaction at the temperature of interstellar clouds. *Science Advances*, 7(2):eabe4080, 2021.
[43] Valentina Zhelyazkova, Fernanda B. V. Martins, Josef A. Agner, Hansjrg Schmutz, and Frdric Merkt. Multipole-moment effects in ionmolecule reactions at low temperatures: part i ion-dipole enhancement of the rate coefficients of the $He^+ + NH_3$ and $He^+ + ND_3$ reactions at collisional energies ecoll/kb near 0 k. *Phys. Chem. Chem. Phys.*, 23:21606–21622, 2021.
[44] Daniel Hauser, Seunghyun Lee, Fabio Carelli, Steffen Spieler, Olga Lakhmanskaya, Eric S Endres, Sunil S Kumar, Franco Gianturco, and Roland Wester. Rotational state-changing cold collisions of hydroxyl ions with helium. *Nature Physics*, 11(6):467–470, 2015.
[45] J. Toscano, H. J. Lewandowski, and B. R. Heazlewood. Cold and controlled chemical reaction dynamics. *Phys. Chem. Chem. Phys.*, 22:9180–9194, 2020.
[46] Brianna R Heazlewood and Timothy P Softley. Towards chemistry at absolute zero. *Nat. Rev. Chem.*, 5(2):125–140, 2021.
[47] Stefan Willitsch, Martin T. Bell, Alexander D. Gingell, and Timothy P. Softley. Chemical applications of laser- and sympathetically-cooled ions in ion traps. *Phys. Chem. Chem. Phys.*, 10:7200–7210, 2008.
[48] Stefan Willitsch. Coulomb-crystallised molecular ions in traps: methods, applications, prospects. *International Reviews in Physical Chemistry*, 31(2):175–199, 2012.
[49] Brianna R. Heazlewood and Heather J. Lewandowski. *Chemistry Using Coulomb Crystals*, chapter 17, pages 389–410.
[50] Richard D. Smith and James J. DeCorpo. A study of the mechanism of (2p) carbon ion reactions with benzene at 1.0 to 12 ev. *J. Phys. Chem.*, 80(26):2904–2910, 1976.
[51] Richard D. Smith and Jean H. Futrell. Reactions of thermal energy (2p) C^+ ions with several molecules. *Int. J. Mass Spectrom. Ion Phys.*, 26(2):111–113, 1978.
[52] R. I. Kaiser, I. Hahndorf, L. C. L. Huang, Y. T. Lee, H. F. Bettinger, P. v. R. Schleyer, H. F. Schaefer, and P. R. Schreiner. Crossed beams reaction of atomic carbon, $C(^3P_j)$, with d6-benzene, C_6D_6 $(X\,^1A_{1g})$: Observation of the per-deutero-1,2-didehydro- cycloheptatrienyl radical, C_7D_5 $(X\,^2B_2)$. *J. Chem. Phys.*, 110:6091–6094, 1999.
[53] D.K. Bohme, A.B. Rakshit, and H.I. Schiff. Reactions of $^{12}C^+$ with hydrocarbons at 296 k:carbon-carbon bond formation. *Chem. Phys. Lett.*, 93(6):592–597, 1982.
[54] G. A. Blake, V. G. Anicich, and Jr. Huntress, W. T. Chemistry of Chlorine in Dense Interstellar Clouds. *Astrophys. J.*, 300:415, January 1986.
[55] O. Asvany, C. R. Markus, K. Nagamori, H. Kohguchi, J. Furuta, K. Kobayashi, S. Schlemmer, and S. Thorwirth. Pure rotational spectrum of CCl^+. *Astrophys. J.*, 910(1):15, mar 2021.
[56] P. C. Schmid, J. Greenberg, M. I. Miller, K. Loeffler, and H. J. Lewandowski. An ion trap time-of-flight mass spectrometer with high mass resolution for cold trapped ion experiments. *Rev. Sci. Instr.*, 88(12):123107, 2017.
[57] J. Greenberg, P. C. Schmid, M. Miller, J. F. Stanton, and H. J. Lewandowski. Quantum-state-controlled reactions between molecular radicals and ions. *Phys. Rev. A*, 98:032702, Sep 2018.
[58] P. C. Schmid, M. I. Miller, J. Greenberg, T. L. Nguyen, J. F. Stanton, and H. J. Lewandowski. Quantum-state-specific reaction rate measurements for the photo-induced reaction $Ca^+ + O_2 \rightarrow CaO^+ + O$. *Mol. Phys.*, 0:1–7, 2019.
[59] P. C. Schmid, J. Greenberg, T. L. Nguyen, J. H. Thorpe, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton, and H. J. Lewandowski. Isomer-selected ion–molecule reactions of acetylene cations with propyne and allene. *Phys. Chem. Chem. Phys.*, 22:20303–20310, 2020.
[60] J. Greenberg, P. C. Schmid, J. H. Thorpe, T. L. Nguyen, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton, and H. J. Lewandowski. Using isotopologues to probe the potential energy surface of reactions of ${C_2H_2}^+ + C_3H_4$. *J. Chem. Phys.*, 154:124310, 2021.
[61] Julian Schmidt, Daniel Hönig, Pascal Weckesser, Fabian Thielemann, Tobias Schaetz, and Leon Karpa. Mass-selective removal of ions from Paul traps using parametric excitation. *App. Phys. B*, 126(11):176, 2020.
[62] C. Q. Jiao, D. R. A. Ranatunga, W. E. Vaughn, and B. S. Freiser. A pulsed-leak valve for use with ion trapping mass spectrometers. *J. Am. Soc. Mass Spectrom.*, 7(1):118–122, 1996.
[63] Yan Zhao and Donald G. Truhlar. The m06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four m06-class functionals and 12 other functionals. *Theor. Chem. Acc.*, 120(1):215–241, 2008.
[64] Thom H Dunning Jr. Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through

neon and hydrogen. *J. Chem. Phys.*, 90(2):1007–1023, 1989.

[65] Rick A Kendall, Thom H Dunning Jr., and Robert J Harrison. Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions. *J. Chem. Phys.*, 96(9):6796–6806, 1992.

[66] David E Woon and Thom H Dunning Jr. Gaussian basis sets for use in correlated molecular calculations. iii. the atoms aluminum through argon. *J. Chem. Phys.*, 98(2):1358–1371, 1993.

[67] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, and J. Olsen. Basis-set convergence of the energy in molecular hartree–fock calculations. *Chem. Phys. Lett.*, 302:437–446, 1999.

[68] Robert M. Parrish, Lori A. Burns, Daniel G. A. Smith, Andrew C. Simmonett, A. Eugene DePrince, Edward G. Hohenstein, Uğur Bozkaya, Alexander Yu. Sokolov, Roberto Di Remigio, Ryan M. Richard, Jérôme F. Gonthier, Andrew M. James, Harley R. McAlexander, Ashutosh Kumar, Masaaki Saitow, Xiao Wang, Benjamin P. Pritchard, Prakash Verma, Henry F. Schaefer, Konrad Patkowski, Rollin A. King, Edward F. Valeev, Francesco A. Evangelista, Justin M. Turney, T. Daniel Crawford, and C. David Sherrill. Psi4 1.1: An Open-Source Electronic Structure Program Emphasizing Automation, Advanced Libraries, and Interoperability. *J. Chem. Theory Comput.*, 13(7):3185–3197, 2017.

[69] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian16 Revision C.01, 2016. Gaussian Inc. Wallingford CT.

[70] B. Weiner, C. J. Williams, D. Heaney, and M. C. Zerner. Structures of ${C_5H_3}^+$. *J. Phys. Chem.*, 94:7001–7007, 1990.

[71] K. Lammertsma and P. v. R. Schleyer. Structures and energies of ${C_6H_6}^{+2}$ isomers. fragmentation into ${C_5H_3}^+$ and ${CH_3}^+$. *J. Am. Chem. Soc.*, 105:1049–1051, 1983.

[72] J. Fulara, A. Chakraborty, A. Nagy, K. Filipkowski, and J. P. Maier. Electronic transitions of ${C_5H_3}^+$ and C_5H_3: Neon matrix and caspt2 studies. *J. Phys. Chem. A*, 119:2338–2343, 2015.