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Reactions of N^+ and $N_2{}^+$ with several cyclic molecules studied using a selected ion flow tube

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ABSTRACT

A selected ion flow tube, SIFT, has been used to investigate the reactions of N^+ and $N_2{}^+$ with four cyclic molecules (pyrrole, pyrrolidine, benzene, and cyclohexane) at 298 K. These species are of particular interest to the chemistry of both Titan's ionosphere and of interstellar molecular clouds. Rate coefficients and product distributions have been determined to provide kinetic data needed for accurate models of these media and establish chemical routes. The majority of reactions proceed at the gas kinetic rate; only pyrrolidine reacts slower. The reactions result mainly in dissociative charge transfer, except the reaction of benzene with N^+, in which the major product is non-dissociative charge transfer. Comparisons are made between each neutral with the two reactant ions (N^+ and $N_2{}^+$) of differing recombination energies and also between each reactant ion with neutrals differing in ionization energy and aromaticity. Fragmentation channels are discussed and compared with electron impact ionization.

1. Introduction

Reactions of cyclic molecules are of interest because many are abundant in interstellar molecular clouds, ISC, and some have also been detected in Titan's atmosphere. Detected ring molecules in ISC include c-C_3H, c-C_3H_2, c-CH_2OCH_2 [1], c-C_2H_3N, c-C_2H_5N [2], c-C_3H_2O [3], as well as C_6H_6 [4] (benzene). Ring compounds identified in Titan's atmosphere are c-$C_3H_3{}^+$ [5], C_6H_6 [6], and c-$C_5H_5N^+$ and/or c-$C_6H_7{}^+$ [7]. Also, polycyclic aromatic hydrocarbons [8], PAHs, and those containing one or more nitrogen atoms, PANHs, are thought to be responsible for unidentified IR emissions [9].

N_2 is the major neutral component of Titan's atmosphere (95% N_2 and 5% CH_4) [10]. It forms $N_2{}^+$ and N^+ when subjected to solar extreme ultra-violet radiation and the energetic electrons of Saturn's magnetosphere, initiating complex chemical reaction sequences [7]. $N_2{}^+$ and N^+ provide the starting point for ionospheric models of Titan's major ion chemistry [5,11,12], including reactions with cyclic molecules, and therefore these are of interest in the present study.

Chemical models are vital for predicting the existence of observed species. Species in ISC are mainly detected by microwave emissions, hence their identity is conclusive. Models of ISC seek to predict abundances of the different species, for comparison with abundances observed, in order to establish chemical routes [13]. In its probing of Titan's atmosphere, the Cassini INMS (Ion Neutral Mass Spectrometer) obtains only mass spectra of ions and neutrals. Models are used to interpret mass spectrometric abundances in terms of molecular identity by comparing those masses detected by Cassini with those predicted by the models [7]. This establishes the chemical routes, but requires a large amount of chemical kinetic data, including both rate coefficients and product distributions.

The present study consists of the reactions of $N_2{}^+$ and N^+ with the neutrals pyrrole (C_4H_5N), pyrrolidine (C_4H_9N), benzene (C_6H_6), and cyclohexane (C_6H_{12}). $N_2{}^+$ and N^+ have large recombination energies (15.58 eV and 14.53 eV) leaving ample energy for fragmentation. Rate coefficients and product distributions are reported, providing some of the data needed for the models.

2. Experimental

The reactions were studied using a selected ion flow tube (SIFT) at 298 K. Details of the technique can be found in the literature [14,15] and this will not be described in depth here. A low pressure ionization source was employed with nitrogen as the source gas to create the primary ions, $N_2{}^+$ and N^+, by electron impact. These ions were then mass selected by a quadrupole mass filter and injected into the flow tube. Here, helium carrier gas transported them downstream to the detection quadrupole/ion counting system. The total pressure in the flow tube was maintained at ~0.5 Torr by the He flow, which was evacuated by a Roots pump after sampling the ions. Ring type injectors introduced the reactant neutral into the flow tube downstream of the ion injection port and after the ions had thermalized by collisions (~10^7) with the He.

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All of the reactant neutrals, used in this study, are liquids at room temperature. Pyrrolidine and pyrrole have low vapor pressures and their vapors tend to stick to the flow tube wall, making accurate determination of flows difficult. To eliminate this obstacle, mixtures were made of these and of the two higher vapor pressure liquids, benzene and cyclohexane [16]. Samples were prepared by evaporating the neat vapors into an evacuated vessel and diluting with helium. Cyclohexane was diluted in a 9.98% mixture while the other three samples were diluted to ~1% mixtures, keeping the reactant pressure less than its saturated vapor pressure to minimize condensation on the vessel walls. Pyrrole apparently readily dimerizes [17], but no evidence for this was seen and the energies associated are unknown. Dimerization would be noticable in that the experimental rate coefficient is likely to be greater than predicted by the calculated theoretical collisional rates. This would occur since the concentration in the mixture of the neutral would be incorrect due to the dimer monomerization after injection.

Sigma–Aldrich provided three of the liquid reactants with quoted purities of 98% for pyrrole, 99.5+% for pyrrolidine, and ≥99% for cyclohexane. Benzene was obtained from Fisher Scientific with a purity of 99.5%. Additional purification of these liquids was achieved by freeze-pump–thaw cycles, removing dissolved gases before use. The high purity helium used for both dilution and as the carrier gas (National Welders Specialty Gases) was passed through a molecular sieve cooled with liquid nitrogen for additional purification before use. Rate coefficients and product distributions were determined in the usual way [14,15,18,19] taking into account the dilution of the reactant neutrals. Rate coefficients are accurate to ±25% and product distributions to ±5 in the percentage. Mass discrimination effects in the detection quadrupole mass filter have been taken into account.

3. Results and discussion

The experimental reaction rate coefficients, k_{exp}, are given in Table 1 as well as the theoretical collisional rate coefficients, k_{theor}, which were determined using parameterized trajectory calculations [20]. Experimental values are quoted from the literature, k_{lit}, where available [21,22]. Our values are within reasonable error of the experimental literature values. The reactions of N_2^+ and N^+ with benzene and N^+ with cyclohexane are the only reactions in this study for which rate coefficients have been previously reported. Most reactions proceed within experimental error of the gas kinetic values except those with pyrrolidine as the reactant neutral. It is unknown why these pyrrolidine reactions are less efficient than the other reactions studied, but reactions with this neutral in another study [23], as well as another in the literature [24], show the same effect. Note that reaction efficiencies and rate coefficients, both experimental and theoretical, are larger for reactant neutrals with π electrons in the ring due to the attractive forces they create with the positive ions.

Table 1
Experimental rate coefficients, k_{exp}, for the reactions of N^+ and N_2^+ with the neutrals listed, along with the theoretical gas kinetic rate coefficients, k_{theor}, established by parameterized trajectory calculations [20], and rate coefficients from the literature [21,22], k_{lit}, included in parentheses when available.

Primary ion	k_{exp} ($\times 10^{-9}$ cm^3 s^{-1})	k_{theor} ($\times 10^{-9}$ cm^3 s^{-1})	Efficiency[a]
Pyrrole (C_4H_5N)			
N^+	3.47	3.31	1.05
N_2^+	3.03	2.53	1.20
Pyrrolidine (C_4H_9N)			
N^+	1.88	3.06	0.61
N_2^+	1.21	2.33	0.52
Benzene (C_6H_6)			
N^+	2.56	2.19(2.00)	1.17
N_2^+	1.85	1.66(1.60)	1.11
Cyclohexane (C_6H_{12})			
N^+	2.04	2.34(2.40)	0.87
N_2^+	1.56	1.69	0.92

Values for polarizability [16,42,43] and dipole moment [24,44] of the neutrals were used to calculate the theoretical gas kinetic rate coefficients.

[a] Reaction efficiency, k_{exp}/k_{theor}.

Table 2
Ion product distributions (%) for reactions between N^+ and N_2^+ and the neutrals listed along with the literature ion product percentages [21,25] in parentheses when available.

Neutral reactant	Ion product	N^+ 14.53 eV %	N_2^+ 15.58 eV %	EI 70 eV %
Pyrrole (C_4H_5N) 8.21 eV	$C_3H_3^+$, C_2HN^+	14	38	16
	$C_3H_4^+$, $C_2H_2N^+$	12	13	13
	$C_3H_5^+$, $C_2H_3N^+$	8	27	15
	$C_4H_4^+$, $C_3H_2N^+$	15	0	<1
	$C_4H_5^+$, $C_3H_3N^+$	15	0	0
	$C_3H_4N^+$	16	0	0
	$C_4H_4N^+$	8	≤5	2
	$C_4H_5N^+$	12	17	24
Pyrrolidine (C_4H_9N) 8.77 eV	$C_2H_6^+$, CH_4N^+	0	10	3
	$C_3H_5^+$, $C_2H_3N^+$	7	13	6
	$C_3H_6^+$, $C_2H_4N^+$	0	23	9
	$C_3H_7^+$, $C_2H_5N^+$	63	45	36
	$C_4H_8N^+$	24	≤2	10
	$C_4H_9N^+$	6	7	7
Benzene (C_6H_6) 9.24 eV	[a]$C_3H_3^+$	22(12)	12(17)	4
	l-$C_4H_4^+$	0(2)	30(36)	
				7
	c-$C_4H_4^+$	0(3)	7(5)	
	$C_5H_3^+$	0	≤3(2)	2
	$C_5H_4^+$	7(7)	0	0
	$C_6H_4^+$	0(1)	6(4)	2
	c-$C_6H_5^+$	0	19	
		(7)	(24)	11
	c-$C_6H_5^+$	0	≤2	
	$C_6H_6^+$	71(68)	21(12)	39
Cyclohexane (C_6H_{12}) 9.80 eV	$C_3H_5^+$	23	51	14
	$C_3H_6^+$	8	6	7
	$C_3H_7^+$	9	≤4	3
	$C_4H_7^+$	19	23	7
	$C_4H_8^+$	28	6	21
	$C_5H_7^+$	0	≤2	<1
	$C_5H_9^+$	≤3	0	5
	$C_6H_{11}^+$	0	≤5	<1
	$C_6H_{12}^+$	10	≤3	15

Ionization energies are given under the neutrals and the recombination energies under the ions [26].

[a] Identified in the literature as c-$C_3H_3^+$.

Ion product distributions for the reactions studied are given in Table 2. The literature product distributions for the benzene reactions with N_2^+ and N^+ and cyclohexane with N_2^+ are included in parentheses and agree reasonably well with our product distributions. None of the other reactions in this study have prior ion product distributions for comparison. Electron impact, EI, ionization abundances are shown for discussion and comparison of the fragmentation channels. Photoionization efficiency, PIE, curves are also useful in predicting expected fragment ions, but the estimated ion abundances do not correlate with those from ion–molecule reactions, consistent with previous observations [21].

The products of the reactions of each neutral with the two reactant ions of differing recombination energy are compared. Reactant neutrals differing in aromaticity (i.e., aromatic benzene versus cyclohexane and aromatic pyrrole versus pyrrolidine) are included in this study. These comparisons are readily seen in Table 3, which gives ΔE, the energy difference between the recombination energy of the reactant ion and the ionization energy of the reactant neutral, and indicates which species are aromatic.

Table 3
Energy differences, number of product channels, and aromaticity of neutrals (as given by Y for yes and N for no) for reactions listed.

Reactants	Energy difference, ΔE^a (eV)	Number of product channels	Neutral aromaticity
Pyrrole (C_4H_5N) 8.21 eV			Y
N^+	6.32	8	
N_2^+	7.37	5	
Pyrrolidine (C_4H_9N) 8.77 eV			N
N^+	5.76	4	
N_2^+	6.81	6	
Benzene (C_6H_6) 9.24 eV			Y
N^+	5.29	3	
N_2^+	6.34	8	
Cyclohexane (C_6H_{12}) 9.80 eV			N
N^+	4.73	7	
N_2^+	5.78	8	

[a] Calculated by subtraction of ionization energy of neutral (listed under each species) from recombination energy of ion (14.53 eV for N^+ and 15.58 eV for N_2^+) [26].

The ΔE values quoted denote the amount of energy left over after the neutral has been ionized by charge transfer which is available to break bonds and fragment the neutral. It is expected that fragmentation products arising from charge transfer will be the same as the products seen following EI ionization of the neutral. However, charge transfer fragmentation abundances will differ due to the narrow distribution of internal energy transferred to the neutral in ion–molecule reactions [25]. If products are seen in ion–molecule reactions which are not seen in the EI spectrum, other channels such as hydride ion abstraction or association are expected to be the precursors prior to fragmentation to yield products.

The reactions result mainly in dissociative charge transfer, except the reaction of benzene with N^+, in which the major product is non-dissociative charge transfer. This result can be explained by the aromatic stability of benzene and the smaller ΔE value of the reaction. N_2^+ has larger recombination energy than N^+, thus giving a larger ΔE value for each neutral, and produces more fragment ions than N^+ in all cases except with pyrrole. Unfortunately, in most cases, the heat of formation of one or more of the possible products is unknown, making definitive assignment of the ion products impossible. However, in a few cases it is possible to calculate the enthalpy of reaction. Production of N_2 in the N^+ reactions with pyrrole and pyrrolidine is exothermic for the possible product channels. This may be a partial explanation of why N^+ reactions with pyrrole produce more fragments than the corresponding N_2^+ reactions, although this effect is not seen in the pyrrolidine reactions. In addition, energetics associated with insertion of reactant ions into the neutral products to form C–N bonds have been examined. Again, unfortunately, just a few of the heats of formation are present in the literature, but where available, only some reactions are exothermic. The major product (m/z 43) for both of the pyrrolidine reactions can be identified as $C_2H_5N^+$ based on known EI fragmentation mechanisms since this m/z appears as the most abundant peak in the EI spectrum.

3.1. *Pyrrole and pyrrolidine*

The pyrrole reactions are unique in this study because the reactant ion with greater recombination energy gives less fragmentation. The products of the reaction with N_2^+ are all in the EI spectrum of pyrrole [26] and can be explained by fragmentation after charge transfer. However, some of the products of the reaction with N^+ cannot. The ion at m/z 52 ($C_4H_4^+$ and/or $C_3H_2N^+$) occurs on pyrrole's EI spectrum with <1% actual abundance compared with the 15% product of the ion–molecule reaction. The difference in the distribution of internal energies can influence abundances for EI versus ion–molecule reactions [25], but also, this product could occur through other channels. Products at m/z values of 53 ($C_4H_5^+$ and/or $C_3H_3N^+$) and 54 ($C_3H_4N^+$) are not found on the EI spectrum and thus probably arise from channels other than charge transfer. Both ion–molecule reactions with pyrrole give products at m/z 40 which could be identified as either $C_3H_4^+$ and/or $C_2H_2N^+$. If this product was $C_3H_4^+$, it could give HCN as the neutral product, which is energetically possible. This is worth noting since HCN is abundant in both ISC and Titan's atmosphere [5,27], and this reaction could provide a small part of the source. Although benzene is the only neutral in this study which has been identified in ISC [4] and Titan's atmosphere [6], the possibility of other homo- and also heterocyclic compounds is likely [9].

All products of the pyrrolidine reactions occur also on the EI spectrum [26]. Therefore, it is reasonable to conclude that all products were formed after charge transfer to the neutral and can be produced by known EI fragmentation mechanisms [25]. Both reactions with pyrrolidine give the major product at m/z 43, which could be $C_3H_7^+$ and/or $C_2H_5N^+$. When pyrrolidine loses an electron by EI ionization, it will most likely be taken from the nitrogen's lone pair since those electrons are in the highest occupied molecular orbital (HOMO) [28]. The same is expected after charge transfer in ion–molecule reactions, placing the radical-site on the nitrogen. Starting here with known EI fragmentation mechanisms, the ion $C_2H_5N^+$ can be assigned to m/z 43 after two consecutive radical-site initiated α cleavage reactions [28].

3.2. *Benzene and cyclohexane*

The benzene reactions in the current study have product distributions that agree reasonably well with the literature. The reaction of benzene with N^+ yields products shown on its EI spectrum [26], except for $C_5H_4^+$, which is only a small product (7%) in this reaction. Thus, it should be formed after ionization by a channel other than charge transfer. All observed products of the reaction with N_2^+, as well as the remaining N^+ products, are considered to result after charge transfer since they are visible on benzene's EI spectrum. It is possible that the products $C_5H_3^+$ and $C_6H_4^+$ are formed via another fragmentation channel because their EI peak abundances are small, although their product abundances in this reaction with N_2^+ are also low. The major product in the reaction of benzene with N_2^+ is $C_4H_4^+$, and this product not seen when reacting benzene with N^+. (Note though that small percentages of both cyclic and linear isomers of $C_4H_4^+$ have been reported in the literature [21].) This could result from the smaller ΔE value and benzene's aromatic stability. The $C_5H_4^+$ product ion of the reaction of benzene with N^+ again gives the neutral product HCN and is energetically feasible. As noted before, the reaction between benzene and N^+ is the only reaction in this series which gives non-dissociative charge transfer as the major product channel. This is consistent with benzene's aromatic stability and the small ΔE value.

Reactions of N_2^+ and N^+ with neutral cyclohexane give similar product ions and distributions. The literature product distribution for the reaction of cyclohexane with N_2^+ has been previously reported [25] and matches well with the current study. Products of both reactions are seen in the EI spectrum for cyclohexane [26]. $C_5H_7^+$ and $C_6H_{11}^+$ have small EI abundances, in agreement with the fact that they are not seen in the reaction with N^+ and may be negligible in the reaction with N_2^+. Additionally, these ions are not reported in the literature product distribution.

3.3. Aromaticity

Aromatic species are more stable than their saturated counterparts. Part of their stability comes from having full bonding molecular orbitals and empty nonbonding and antibonding molecular orbitals. Taking away or adding an electron will destabilize the compound. Another stabilizing characteristic is the delocalization of electrons in the π system. This effect can be seen by examining the compound's resonance contributors.

Pyrrole and pyrrolidine have the same ring structure but differ in aromaticity. Pyrrole has six π electrons which are delocalized in a conjugated ring. The structure of pyrrole is not simple; instead it is described by five contributing resonance structures. The lone pair on the nitrogen is included in this aromatic system and nitrogen is given a partial positive charge as a result of this delocalization. One measure of aromaticity is a compound's resonance energy. Large resonance energies indicate stability and that the resonance contributors are more equivalent [29]. Resonance energy can be determined by comparing the experimental heat of hydrogenation of the molecule with a calculated heat of hydrogenation of a molecule which has isolated double bonds [30]. For pyrrole, the resonance energy is approximately 88 kJ/mol [29]. This can account for some of the difference in reactivity of pyrrole and pyrrolidine. In comparing the pyrrolidine reactions to the pyrrole reactions, one would expect the pyrrole reactions to produce less fragment ions since pyrrole is aromatic, but the opposite occurs when N^+ is the reactant ion, which may be due to the smaller ΔE value of the reaction of N^+ with pyrrolidine. The pyrrole reactions have slightly larger non-dissociative charge transfer product percentages than the corresponding pyrrolidine reactions, which is expected based on aromaticity arguments.

Benzene and cyclohexane also have the same ring structure, differing in aromaticity. Benzene's six π electrons are delocalized through two equivalent resonance contributors, giving 151 kJ/mol of resonance energy [29]. Benzene fragments less upon reaction, which is expected by its aromaticity, and gives much larger non-dissociative charge transfer product percentages than the same reactions with cyclohexane.

3.4. Isomers

When looking at the data from the reaction of benzene with $N_2{}^+$, product ions $C_4H_4{}^+$ and $C_6H_5{}^+$ showed indications of being composed of two isomers, one reactive and one unreactive with neutral benzene. The counts of each product increased and then began decreasing until a constant signal remained. To determine the product percentages of each isomer, a kinetic model was fitted to the data according to the integrated rate laws given by the following equations:

$$[N_2{}^+] = [N_2{}^+]_0 \exp(-k_1[C_6H_6]t) \tag{1}$$

$$[c\text{-}C_6H_5{}^+] = f_s[N_2{}^+]_0(1 - \exp(-k_1[C_6H_6]t)) \tag{2}$$

$$[l\text{-}C_6H_5{}^+] = \frac{k_1 f_l [N_2{}^+]_0}{k_2 - k_1}(\exp(-k_1[C_6H_6]t) - \exp(-k_2[C_6H_6]t)) \tag{3}$$

In these equations, [] denotes the concentration. The rate coefficient of the initial reaction of $N_2{}^+$ with benzene is given as k_1, which includes f_l and f_s as the product fractions of reactive and unreactive isomers produced. The rate coefficient k_2 is for the further reaction of one of the isomers with benzene. The variables k_1, k_2, f_l, and f_s were changed until the modeled curve fitted the experimental data. An example of this situation is given in Fig. 1. Although this effect was not seen in the literature for $C_6H_5{}^+$ [21], we observed differing reactivities with benzene and were able to determine the percentages of the reactive versus unreactive isomers of $C_6H_5{}^+$. Despite the fact that we were unable to determine these structures experimentally, we assume the reactive isomer is the lower energy phenylium ion based on its reactivity with other hydrocarbons [31,32].

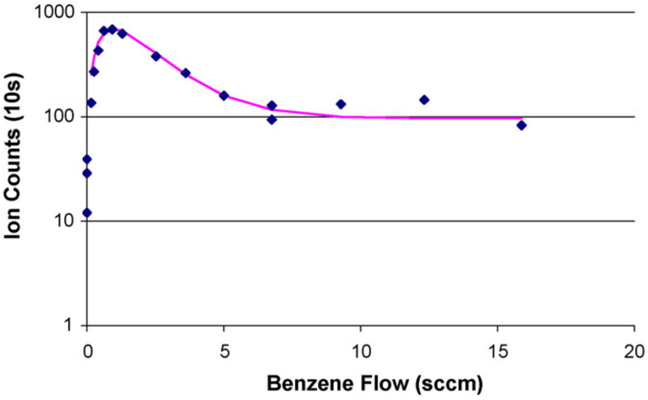

Fig. 1. Behavior of the $C_6H_5{}^+$ ion product from the reaction of $N_2{}^+$ with benzene illustrating two isomeric forms and the modeled curve.

Similar equations were used to find product percentages of the $C_4H_4{}^+$ isomers. For the linear $C_4H_4{}^+$ isomer, vinyl acetylene ion, it has been established that there is a reaction whereas for the cyclic isomer, methylene cyclopropene ion, there is none [33].

4. Conclusions

The current study includes reactions with primary ions $N_2{}^+$ and N^+, which are produced from the major neutral component of Titan's atmosphere, N_2, and gives kinetic data useful for modelers. In Titan's atmosphere, the H_2 present [5] rapidly reacts with $N_2{}^+$ [14,19,34–36] and therefore its reactions are more relevant in ISC. However, N^+ does not react with H_2 due to the large reaction barrier [37,38], so its chemistry is important in modeling Titan's ionosphere. Most of the reactions give many assorted fragmentation products, but there are some common ion products with sizable abundances. The ion product at m/z 41 ($C_3H_5{}^+$ and/or $C_2H_3N^+$) is observed in all studied reactions except for those with benzene. This m/z has been detected in Titan's atmosphere and is presumed to be $C_3H_5{}^+$ [7]. The assignment is logical since $C_3H_5{}^+$ does not react with H_2 or CH_4 [39,40] and $C_2H_3N^+$ will accept a proton from both species [41]. Common ions in the reactions of pyrrole and benzene are those at m/z 39 ($C_3H_3{}^+$ and/or C_2HN^+). This m/z has also been noted in Titan's ionosphere and is believed to be $C_3H_3{}^+$ [7]. The possibility of C_2HN^+ contributing to the ion density is not established because its reactions with H_2 and CH_4 have so far not been studied. The neutral HCN produced in reactions of $N_2{}^+$ with pyrrole and N^+ with both pyrrole and benzene is significant since this neutral is an important part of the chemistry of Titan and ISC and these reactions could provide partial sources. Benzene has been identified in both ISC [4] and Titan's atmosphere [6]. Pyrrole has yet to be detected, but PANHs are thought to be responsible for unidentified IR emissions [9] so the possibility of finding pyrrole is promising.

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References

[1] www.cv.nrao.edu/~awootten/allmols.html, The 129 reported interstellar and circumstellar molecules, 2005.
[2] Y.-J. Kuan, S.B. Charnley, H.-C. Huang, Z. Kisiel, P. Ehrenfreund, W.-L. Tseng, C.-H. Yan, Adv. Space Res. 33 (2004) 31.
[3] J.M. Hollis, A. Remijan, P.R. Jewell, F.J. Lovas, Ap. J. 642 (2006) 933.

[4] http://physics.nist.gov/PhysRefData/Micro/Html/tab2.html, NIST Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions, 2004.
[5] C.N. Keller, V. Anicich, T.E. Cravens, Planet. Space Sci. 46 (1998) 1157.
[6] J.H. Waite, H. Nieman, R.V. Yelle, W.T. Kasprzak, T.E. Cravens, J.G. Luhmann, R.L. McNutt, W.-H. Ip, D. Gell, V. de la Haye, I. Muller-Wordag, B. Magee, N. Borggren, S. Ledvina, G. Fletcher, E. Walter, R. Miller, S. Scherer, R. Thorpe, J. Xu, B. Block, K. Arnett, Science 308 (2005) 982.
[7] T.E. Cravens, I.P. Robertson, J.H. Waite, R.V. Yelle, W.T. Kasprzak, C.N. Keller, S.A. Ledvina, H.B. Nieman, J.G. Luhmann, R.L. McNutt, W.-H. Ip, V. de la Haye, I. Mueller-Wodarg, J.-E. Wahlund, V.G. Anicich, V. Vuitton, Geophys. Res. Lett. 33 (2006) L07105.
[8] D.K. Bohme, Chem. Rev. 92 (1992) 1487.
[9] D.M. Hudgins, C.W. Bauschlicher, L.J. Allamandola, Ap. J. 632 (2005) 316.
[10] S. Atreya, Science 316 (2007) 843.
[11] T.E. Cravens, J. Vann, J. Clark, J. Yu, C.N. Keller, C. Brull, Adv. Space Res. 33 (2004) 212.
[12] V. Vuitton, R.V. Yelle, Ap. J. 647 (2006) L175.
[13] T.J. Millar, E. Herbst, R.P.A. Bettens, Mon. Not. R. Astron. Soc. 316 (2000) 195.
[14] N.G. Adams, D. Smith, Int. J. Mass Spectrom. Ion Phys. 21 (1976) 349.
[15] N.G. Adams, A.D. Smith, in: J.M. Farrar, J.W.H. Saunders (Eds.), Techniques for the Study of Ion-Neutral Reactions, Wiley–Interscience, New York, 1988, p. 165.
[16] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, Inc., New York, 1996–1997.
[17] G. Columberg, A. Bauder, J. Chem. Phys. 106 (1997) 504.
[18] D. Smith, N.G. Adams, in: D.R. Bates, B. Bederson (Eds.), Advances in Atomic and Molecular Physics, Academic Press, New York, 1988, p. 1.
[19] N.G. Adams, D. Smith, J. Phys. B 9 (1976) 1439.
[20] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[21] S.T. Arnold, S. Williams, I. Dotan, A.J. Midey, R.A. Morris, A.A. Viggiano, J. Phys. Chem. A 103 (1999) 8421.
[22] C. Rebrion, J.B. Marquette, B.R. Rowe, N.G. Adams, D. Smith, Chem. Phys. Lett. 136 (1987) 495.
[23] L.D. Fondren, N.G. Adams, L. Stavish, J. Phys. Chem. A, in press.
[24] J. Sun, D.K. Bohme, Int. J. Mass Spectrom. 195/196 (2000) 401.
[25] A.G. Harrison, Chemical Ionization Mass Spectrometry, 2nd ed., CRC Press, Boca Raton, 1992.
[26] http://webbook.nist.gov/chemistry, NIST Chemistry WebBook NIST Standard Database 69.
[27] T. Hirota, Ap. J. 503 (1998) 717.
[28] F.W. McLafferty, F. Turecek, Interpretation of Mass Spectra, 4th ed., University Science Books, Sausalito, 1993.
[29] P.Y. Bruice, Organic Chemistry, 4th ed., Pearson Education, Inc., Upper Saddle River, NJ, 2004.
[30] E.V. Anslyn, D.A. Dougherty, Modern Physical Organic Chemistry, University Science Books, Sausalito, CA, 2006.
[31] P. Ausloos, S.G. Lias, T.J. Buckley, E.E. Rogers, Int. J. Mass Spectrom. Ion Processes 92 (1989) 65.
[32] G.B.I. Scott, D.A. Fairley, C.G. Freeman, M.J. McEwan, N.G. Adams, L.M. Babcock, J. Phys. Chem. A 107 (1997) 4973.
[33] P. Ausloos, J. Am. Chem. Soc. 103 (1981) 3931.
[34] N.G. Adams, D. Smith, J.F. Paulson, J. Chem. Phys. 72 (1980) 288.
[35] D. Smith, N.G. Adams, T.M. Miller, J. Chem. Phys. 69 (1978) 308.
[36] M. Tichy, A.B. Rakshit, D.G. Lister, N.D. Twiddy, N.G. Adams, D. Smith, Int. J. Mass Spectrom. Ion Phys. 29 (1979) 231.
[37] N.G. Adams, D. Smith, T.J. Millar, Mon. Not. R. Astron. Soc. 211 (1984) 857.
[38] S.-h. Ge, Icarus 183 (2006) 153.
[39] V. Anicich, M.J. McEwan, Planet. Space Sci. 45 (1997) 897.
[40] M.J. McEwan, G.B.I. Scott, V. Anicich, Int. J. Mass Spectrom. Ion Processes 172 (1998) 209.
[41] T.W. Martin, C.E. Melton, J. Phys. Chem. 32 (1960) 700.
[42] http://www.chemspider.com, Building a Structure Centric Community for Chemists, 2008.
[43] M.T. Rodgers, Wayne State University, 2008.
[44] http://srdata.nist.gov/cccbdb, NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 14.