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An experimental survey of the reactions of NH_n^+ ions ($n=0$ to 4) with several diatomic and polyatomic molecules at 300 K^{a)}

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A study has been made of the binary reactions at 300 K in a SIFT apparatus of the ions N^+ , NH^+ , NH_2^+ , NH_3^+ , and NH_4^+ with CH_3NH_2 , NO , NH_3 , H_2S , CH_3OH , H_2CO , COS , O_2 , H_2O , CH_4 , CO_2 , CO , H_2 , and N_2 . The N^+ , NH^+ , and NH_2^+ reactions are generally fast, their rate coefficients being close to the collisional limit, and multiple product channels result, especially for reactions with the polyatomic molecules. Several reaction mechanisms are apparent, including charge transfer, proton transfer, and H-atom abstraction, although it is argued that many of the reactions proceed via a short-lived, ion-molecule complex which separates along the observed reaction channels. The NH_3^+ ions are seen to be generally less reactive than the lesser hydrogenated ions, the product of most of the reactions being NH_4^+ ions which do not undergo binary reactions with any of the molecules (except CH_3NH_2) but rather undergo ternary association reactions with a few of them. A few measurements were made using the deuterated analogs ND^+ , ND_2^+ , ND_3^+ , and ND_4^+ in order to shed further light on some of the reaction mechanisms.

I. INTRODUCTION

Insight into the mechanisms by which ion-molecule reactions proceed at thermal energies has been obtained by studying the variations of their rate coefficients with temperature and ion kinetic energy. Additional information can be obtained from studies of the reactions of a series of atomic and molecular ions of varying complexity and recombination energy. To this end, we have recently studied in detail the reactions at 300 K of the ion sequences N_n^+ ($n=0$ to 4),¹ CH_n^+ ($n=0$ to 4),²⁻⁵ and H_nCO^+ ($n=0$ to 3)⁶ with several molecules of varying complexity. These studies have provided not only the rate coefficients for the reactions but also accurate product ion distributions and through the latter have revealed that considerable bond breaking and bond formation occurs in thermal energy ion-molecule reactions. This implies that during the "collision" between the positive ion and neutral molecule, a "short-lived complex" is almost invariably formed and that long-range charge (electron) transfer or simple heavy particle (e.g., proton) transfer rarely occurs at thermal energies in these systems. As a further contribution to this field of research, we report here the results of a study of the reactions of the successively hydrogenated ions N^+ , NH^+ , NH_2^+ , NH_3^+ , and NH_4^+ with 14 molecules of varying complexity (diatomic to 7 atomic). Additional motivation for the choice of the particular ionic and neutral molecular species in this study relates to our continuing interest in the role of gas phase ion-molecule reactions in the synthesis of the molecules observed in interstellar gas clouds. However, a discussion of the significance of the present data to interstellar cloud ion chemistry is more properly the subject of a separate paper.

II. EXPERIMENTAL

The data presented in this paper have been obtained using a selected ion flow tube (SIFT) apparatus at 300 K. The basic SIFT, which has been exploited to determine a large number of rate coefficients and product ion distributions of thermal energy ion-molecule reactions, has been described in detail elsewhere.^{7,8} Much of the data relating to the wide variety of reactions studied to date have been summarized in a recent review,⁹ together with a description of our recently constructed, more sophisticated SIFT which has been used in the present study. The SIFT technique, in essence, involves the generation of ions in some form of ion source, mass selection of a particular ionic species using a quadrupole mass filter, and the injection of the resulting ion "beam" at low energy into a flowing helium carrier gas. The ions are convected downstream in the flowing helium gas and are detected by a sampling orifice/mass filter/ion detection and counting system. Reactions are studied by adding the reactant gas at a position downstream of the ion injection point while the reactant and product ion count rates are recorded as a function of the reactant gas flow rate (see as examples Figs. 1-3). From these data, the rate coefficients and product ion distributions for the reactions are determined (see Sec. III).

The positive ions of interest here were generated in a low pressure electron impact ion source (electron energy ~ 70 eV) containing ammonia at a pressure of ~ 1 mtorr. Thus, adequate currents of NH^+ , NH_2^+ , and NH_3^+ ions were generated, but the current of NH_4^+ was much smaller since it obviously cannot be produced by ionization of NH_3 . This ion is formed via the secondary reaction of NH_3^+ with NH_3 which proceeds only slowly at the maximum pressure that can be tolerated in the ion source and hence in the injection quadrupole chamber to which it is directly coupled.

Although only one N^+ ion reaction (i.e., with NO) was

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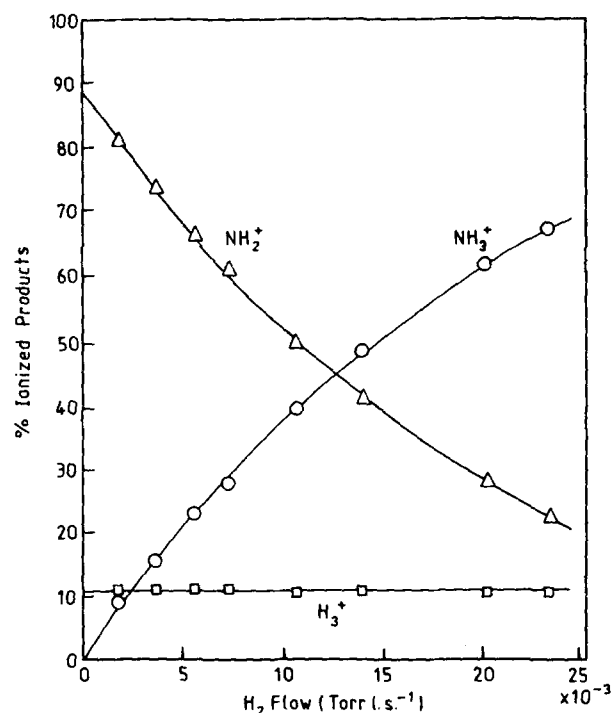
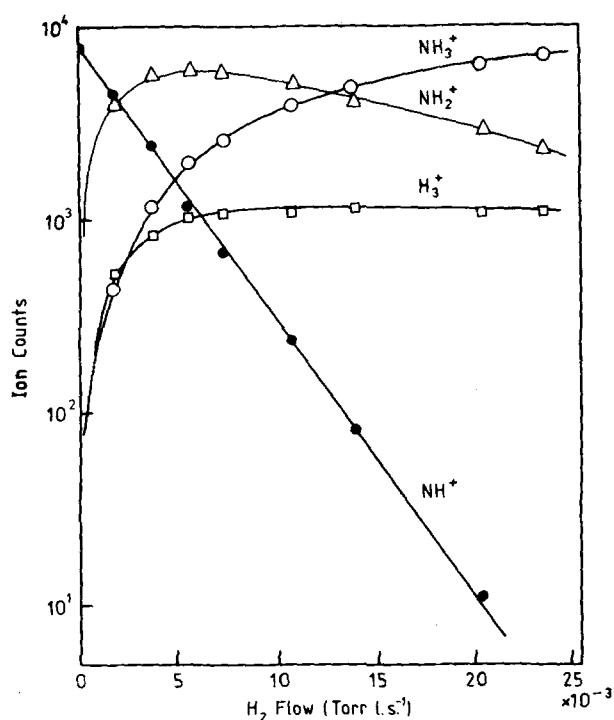


FIG. 1. Variation with H_2 flow of (a) the primary and product ion counts (10 s sampling period) and (b) the percentages of the ionized products for the reaction of NH^+ with H_2 at 300 K. In these figures, no account has been taken of the relatively greater diffusive loss of H_3^+ . Detailed analysis to account for this effect gives the product distribution (NH_2^+ , 85%; H_3^+ , 15%) quoted in Table I. NH_3^+ is clearly a secondary product ion only.

included in this study (we have studied the reactions of N^+ ions with the other reactant molecules included in this study in a previous SIFT programme of measurements¹), it is nevertheless worth briefly mentioning the source configuration used to generate the N^+ ions since it highlights a potential problem when low pressure,

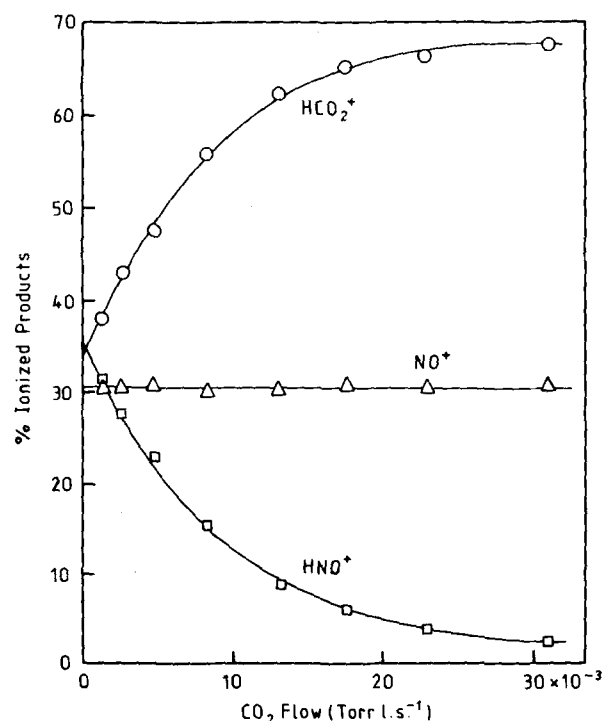
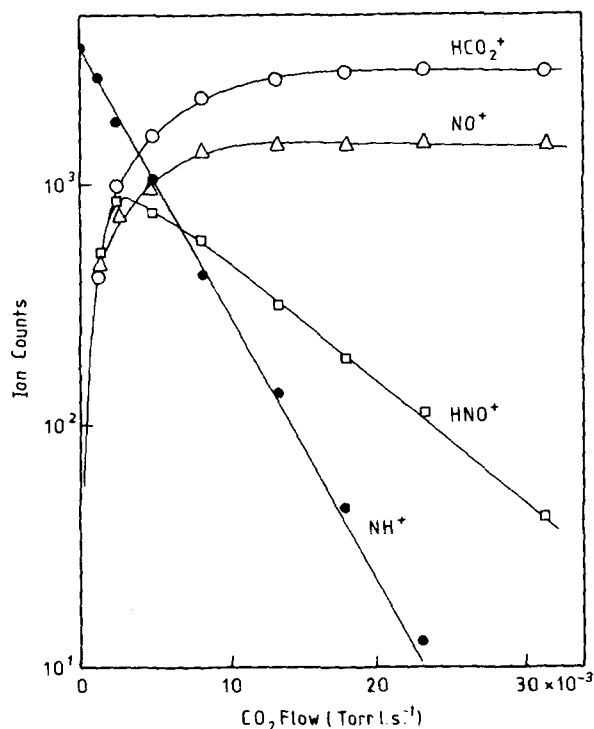


FIG. 2. Variation with CO_2 flow of (a) the primary and product ion counts (10 s sampling period) and (b) the percentages of the ionized products for the reaction of NH^+ with CO_2 at 300 K. Figure 2(b) graphically illustrates the secondary reaction of the primary product ion HNO^+ with CO_2 which produces HCO_2^+ . Thus, HCO_2^+ is both a primary and a secondary product ion.

electron impact, ion sources are used. Nitrogen was used as the source gas, but for 70 eV electrons significant concentrations of N_2^{+} ($m/e=14$) and metastable electronically excited N^+ ions were generated and injected into the flow tube, clearly a most undesirable situation which confuses the data interpretation. (In

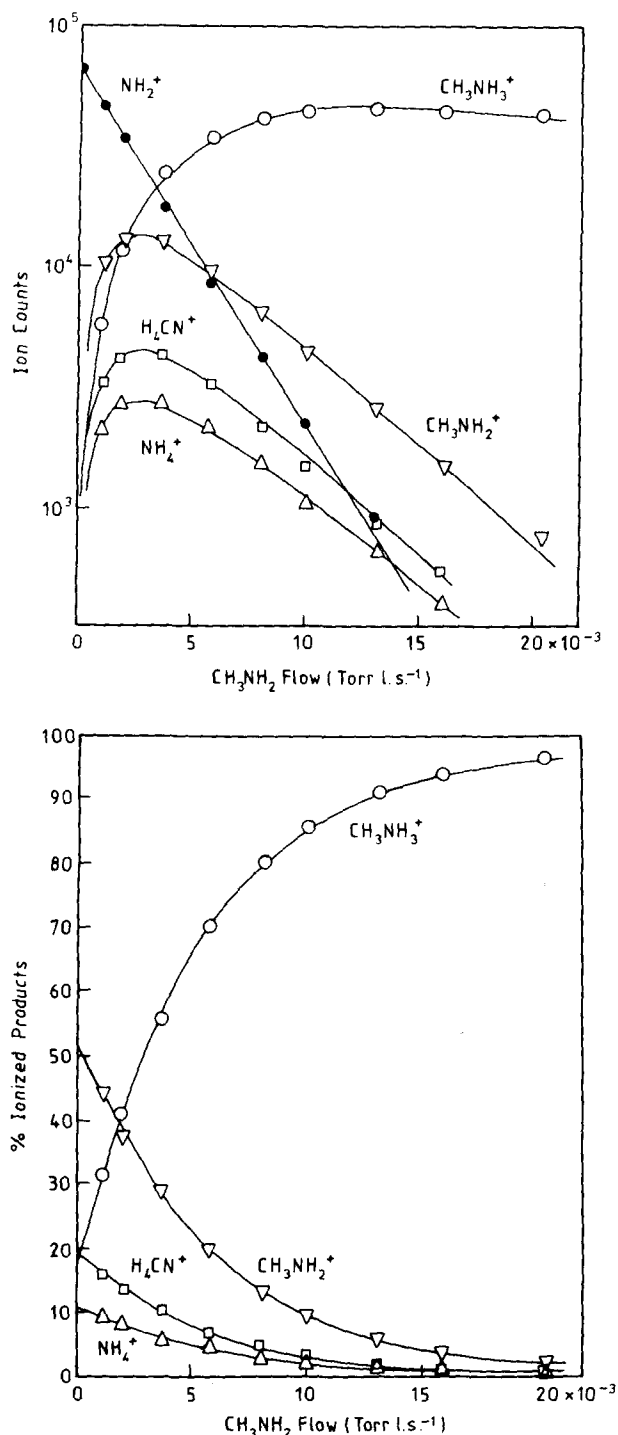


FIG. 3. Variation with CH_3NH_2 flow of (a) the primary and product ion count rates (10 s sampling period) and (b) the percentages of the ionized products for the reaction of NH_2^+ with CH_3NH at 300 K. CH_3NH_3^+ is evidently both a primary product ion and a secondary product ion.

fact, we have previously exploited this phenomenon by determining the rate coefficients and product ion distributions for reactions of several metastable excited ions^{10,11}). For electron energies ≤ 40 eV, the doubly charged ions and excited ions were effectively absent; the checks undertaken to ensure this have been discussed in our previous publications.^{1,11} No such problems were apparent for the other primary reactant ions used in this

study; at least no energetically unacceptable product channels were observed for the many reactions of each ion for which accurate ergicities can be calculated. Thus, all of the data presented in this paper refer to ground state reactant ions.

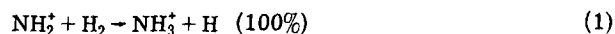
The reactant vapors H_2O and CH_3OH were introduced into the SIFT from reservoirs containing prepared mixtures of the vapors with helium in accurately known proportions.⁶ The H_2CO was produced by thermal decomposition of paraformaldehyde.⁶

III. RESULTS

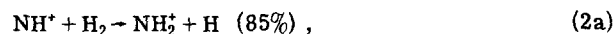
The 14 molecules adopted for this study are given in Table I. As can be seen, they vary greatly in complexity and reactivity, ranging from the relatively stable and unreactive N_2 to the much more reactive CH_3NH_2 . They possess significantly different ionization potentials (ranging from 8.97 to 15.58 eV) and proton affinities (4.34 to 9.37 eV). Together with the significant differences in the recombination energies (10.17 to 14.55 eV) and proton detachment energies (4.21 to 8.98 eV) of the reactant ions, these differences lead us to expect wide variations in the types of reactions observed, at least as viewed from the standpoint of the energetics. The critical constants referred to above for each ion and molecule are given in Table I together with the rate coefficients and product ion distributions obtained in this study for each ion-molecule reaction.

As expected, considerable variations were apparent in the many reactions studied, especially in the number of product ions observed in the reactions. It is sufficient to discuss in detail three reactions from this extensive list, in order to illustrate some common features of all the data as well as their wide ranging complexity.

A typical example of the raw data obtained for a reaction which is readily studied in a SIFT is given in Fig. 1(a). The accumulated ion counts over a 10 s period for the primary ion NH^+ and the product ions H_3^+ , NH_2^+ , and NH_3^+ are plotted semilogarithmically as a function of the H_2 reactant gas flow rate. The primary ion decay curve is seen to be linear over greater than two orders of magnitude in count rate, the slope providing a value for the rate coefficient for the reaction $\text{NH}^+ + \text{H}_2$ at 300 K ($1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). The question is whether all three of the ions generated in the flow tube are products of the primary reaction. This is readily resolved by reference to Fig. 1(b), in which the percentage contribution of each ion count rate to the total count rate is plotted as a function of the reactant gas flow rate. That NH_3^+ is a secondary ion produced via the fast binary reaction (see Table I)



is inferred from the zero percentage of NH_3^+ indicated for zero H_2 flow (extrapolated), whereas the finite percentages of NH_2^+ and H_3^+ indicate that both these ions are primary products of the reaction; thus,



So, in this relatively simple reaction, both H-atom ab-

TABLE I. Rate coefficients and product ion distributions for the reactions of N^+ , NH^+ , NH_2^+ , and NH_3^+ with a series of molecules at 300 K. The reactant ions and molecules are arranged in order of their recombination energies and ionization potentials, respectively, the magnitudes of which are indicated in eV below each reactant species. The proton detachment energies for the ions and proton affinities for the neutral molecules are indicated in eV above each reactant species. The reactions of NH_4^+ were also studied but because of the low reactivity of this ion, these data are not included in the table but are discussed in the text. The binary rate coefficients are indicated as, for example, $1.0(-9)$ representing $1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The percentage of each ion product is given in round brackets after the product ion and the Langevin or ADO theoretical rate coefficient^{17,18} for each reaction is given in square brackets below the experimentally determined value. The N^+ reactions were investigated in a previous study¹ except for that with NO , which is part of the present study, and have been included here for comparison. The ternary rate coefficient ($\text{cm}^6 \text{ s}^{-1}$) is quoted for the $\text{N}^+ + \text{N}_2$ reaction.

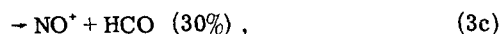
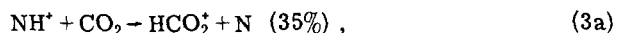
	N^+ 14.55 eV	4.2 eV NH^+ 13.10 eV	6.1 eV NH_2^+ 11.4 eV	8.0 eV NH_3^+ 10.17 eV
9.4 eV CH_3NH_2 8.97 eV	$\text{H}_4\text{CN}^+(70)$, $\text{H}_2\text{CN}^+(10)$ $\text{CH}_3\text{NH}_2^+(7)$, $\text{H}_3\text{CN}^+(7)$ $\text{CH}_3^+(6)$ 2.0(-9) [2.21(-9)]	$\text{H}_4\text{CN}^+(45)$, $\text{CH}_3\text{NH}_2^+(20)$ $\text{CH}_3\text{NH}_3^+(20)$, $\text{H}_2\text{CN}^+(20)$ $\text{H}_3\text{CN}^+(5)$ 2.1(-9) [2.15(-9)]	$\text{CH}_3\text{NH}_2^+(50)$, $\text{CH}_3\text{NH}_3^+(20)$ $\text{H}_4\text{CN}^+(20)$, $\text{NH}_4^+(10)$ 1.8(-9) [2.11(-9)]	$\text{CH}_3\text{NH}_2^+(50)$ $\text{CH}_3\text{NH}_3^+(35)$ $\text{NH}_4^+(15)$ 1.8(-9) [2.06(-9)]
5.0 eV NO 9.25	$\text{NO}^+(85)$ $\text{N}_2^+(15)$ 5.3(-10) [9.99(-10)]	$\text{NO}^+(80)$ $\text{N}_2\text{H}^+(20)$ 8.9(-10) [9.76(-10)]	$\text{NO}^+(100)$ 7.0(-10) [9.55(-10)]	$\text{NO}^+(100)$ 7.2(-10) [9.37(-10)]
9.0 eV NH_3 10.17 eV	$\text{NH}_3^+(82)$ $\text{N}_2\text{H}^+(9)$ $\text{NH}_2^+(9)$ 2.4(-9) [2.32(-9)]	$\text{NH}_3^+(75)$ $\text{NH}_4^+(25)$ 2.4(-9) [2.28(-9)]	$\text{NH}_4^+(70)$ $\text{NH}_3^+(30)$ 2.3(-9) [2.24(-9)]	$\text{NH}_4^+(100)$ 2.2(-9) [2.21(-9)]
7.4 eV H_2S 10.42 eV	$\text{H}_2\text{S}^+(56)$, $\text{SH}^+(29)$ $\text{S}^+(12)$, $\text{NH}^+(3)$ 1.9(-9) [1.86(-9)]	$\text{H}_2\text{S}^+(55)$, $\text{H}_2\text{NS}^+(15)$ $\text{SH}^+(15)$, $\text{HNS}^+(15)$ 1.7(-9) [1.82(-9)]	$\text{H}_2\text{S}^+(40)$, $\text{NH}_3^+(25)$ $\text{H}_3\text{S}^+(15)$, $\text{NH}_4^+(10)$ $\text{SH}^+(10)$ 1.8(-9) [1.78(-9)]	$\text{NH}_4^+(100)$ 1.3(-9) [1.74(-9)]
7.9 eV CH_3OH 10.85 eV	$\text{CH}_3\text{OH}^+(40)$, $\text{H}_2\text{CO}^+(\sim 30)$ $\text{H}_3\text{CO}^+(16)$, $\text{NO}^+(\sim 10)$ $\text{CH}_3^+(4)$ 3.1(-9) [2.42(-9)]	$\text{H}_3\text{CO}^+(70)$, $\text{HCO}^+(15)$ $\text{CH}_3\text{OH}_2^+(10)$, $\text{H}_2\text{CO}^+(15)$ 3.0(-9) [2.36(-9)]	$\text{CH}_3\text{OH}_2^+(85)$ $\text{NH}_3^+(15)$ 3.1(-9) [2.31(-9)]	$\text{NH}_4^+(100)$ 2.2(-9) [2.26(-9)]
7.2 eV H_2CO 10.9 eV	$\text{H}_2\text{CO}^+(\sim 65)$ $\text{HCO}^+(25)$ $\text{NO}^+(\sim 10)$ 2.9(-9) [2.92(-9)]	$\text{HCO}^+(55)$ $\text{H}_2\text{CO}^+(30)$ $\text{H}_3\text{CO}^+(15)$ 3.3(-9) [2.85(-9)]	$\text{H}_3\text{CO}^+(80)$ $\text{NH}_3^+(20)$ 2.8(-9) [2.79(-9)]	$\text{NH}_4^+(100)$ 1.1(-9) [2.74(-9)]
6.2-7.4 eV COS 11.17 eV	$\text{COS}^+(73)$ $\text{S}^+(22)$ $\text{CS}^+(5)$ 1.4(-9) [1.89(-9)]	$\text{COS}^+(85)$, $\text{NS}^+(5)$ $\text{SH}^+(5)$, $\text{HCOS}^+(5)$ 1.8(-9) [1.84(-9)]	$\text{H}_2\text{NS}^+(80)$ $\text{H}_2\text{NCO}^+(15)$ $\text{HCOS}^+(5)$ 1.5(-9) [1.79(-9)]	$\sim 2(-12)$ [1.74(-9)]
4.3 eV O_2 12.06 eV	$\text{O}_2^+(51)$ $\text{NO}^+(43)$ $\text{O}^+(6)$ 6.1(-10) [9.49(-10)]	$\text{O}_2^+(55)$ $\text{NO}^+(25)$ $\text{HO}_2^+(20)$ 8.2(-10) [9.27(-10)]	$\text{H}_2\text{NO}^+(85)$ $\text{HNO}^+(15)$ 1.4(-10) [9.07(-10)]	$< 5(-13)$ [8.87(-10)]
7.2 eV H_2O 12.61 eV	$\text{H}_2\text{O}^+(100)$ 2.8(-9) [2.50(-9)]	$\text{H}_3\text{O}^+(30)$, $\text{H}_2\text{O}^+(30)$ $\text{NH}_2^+(25)$, $\text{HNO}^+(10)$ $\text{NH}_2^+(5)$ 3.5(-9) [2.46(-9)]	$\text{H}_3\text{O}^+(95)$ $\text{NH}_4^+(5)$ 2.9(-9) [2.42(-9)]	(NH_4^+) $\leq 3(-11)$ [2.38(-9)]
5.5 eV CH_4 12.70 eV	$\text{CH}_3^+(51)$, $\text{H}_2\text{CN}^+(40)$ $\text{HCN}^+(6)$, $\text{CH}_4^+(3)$ 9.4(-10) [1.38(-9)]	$\text{H}_2\text{CN}^+(70)$ $\text{NH}_2^+(20)$ $\text{CH}_3^+(10)$ 9.6(-10) [1.36(-9)]	$\text{NH}_3^+(100)$ 9.2(-10) [1.33(-9)]	$\text{NH}_4^+(100)$ 4.8(-10) [1.31(-9)]

TABLE I (Continued)

	N^+ 14.55 eV	4.2 eV NH^+ 13.10 eV	6.1 eV NH_2^+ 11.4 eV	8.0 eV NH_3^+ 10.17 eV
5.4 eV CO_2 13.77 eV	$\text{CO}_2^+(75)$ $\text{CO}^+(25)$	$\text{HCO}_2^+(35)$ $\text{HNO}^+(35)$ $\text{NO}^+(30)$		
	1.0(-9) [1.16(-9)]	1.1(-9) [1.13(-9)]	<1(-12) [1.10(-9)]	<1(-13) [1.08(-9)]
6.1 eV CO 14.01	$\text{CO}^+(88)$ $\text{NO}^+(12)$	$\text{NCO}^+(55)$ $\text{HCO}^+(45)$	$\text{NH}_2^+ \cdot \text{CO} + \text{He}(100)$ pressure independent 0.22-0.52 Torr	
	4.5(-10) [1.08(-9)]	9.8(-10) [1.05(-9)]	2.4(-11) [1.03(-9)]	<5(-13) [1.01(-9)]
4.3 eV H_2 15.43 eV	$\text{NH}^+(100)$	$\text{NH}_2^+(85)$ $\text{H}_3^+(15)$	$\text{NH}_3^+(100)$	(NH_4^+)
	4.8(-10) [1.59(-9)]	1.5(-9) [1.58(-9)]	2.7(-10) [1.58(-9)]	<5(-13) [1.57(-9)]
5.0 eV N_2 15.58 eV	$\text{N}_3^+ + \text{He}(100)$ 5.2(-30)	$\text{N}_2\text{H}^+(100)$ 6.5(-10) [9.94(-10)]	<5(-13) [9.73(-10)]	<5(-14) [9.55(-10)]

straction (2a) and proton transfer (2b) apparently occur, the more exoergic channel (2a) being favored. Although Reaction (2) has been studied previously in a flowing afterglow¹² and an ion cyclotron resonance (ICR) experiment,¹³ significantly, the minor channel (2b) was not observed, presumably because the presence of other ions and reactant gases confused somewhat the product ion spectrum, thus preventing the positive identification of minority products. It is certain that with NH_3 present in the ICR cell, rapid proton transfer from the H_3^+ product ion to the NH_3 would occur,¹⁴ whereas because the H_3^+ is essentially unreactive with H_2 (see Fig. 1) and NH_3 is absent, it is readily observed in this SIFT experiment.

Presented in Fig. 2 is the data for the $\text{NH}^+ + \text{CO}_2$ reaction. Again, three ion species are generated either as primary or secondary reaction products. However, in this case, it is clear from Fig. 2(b) that all three ions HCO_2^+ , HNO^+ , and NO^+ are primary product ions:



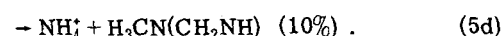
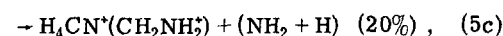
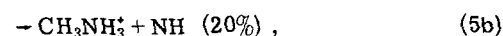
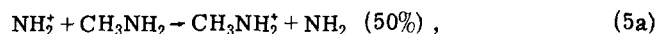
but it is also clear from Fig. 2(b) that the HCO_2^+ is also a product of the rapid secondary reaction



Thus, HCO_2^+ is generated via both of the two proton transfer reactions (3a) and (4). However, Reaction (3) is best considered as proceeding via a coalescence of the ion and molecule in which bond breaking and bond making takes place before unimolecular decomposition into the three observed exit channels occurs, the "proton transfer" channel (3a) being just one of the three options. This is the general picture which is emerging from our detailed studies of thermal energy ion-molecule reactions. It is an interesting and common feature

of many of the reactions studied here that a particular ion (in this case HCO_2^+) is both a product of the primary reaction (3a) and also a product of the secondary reaction of another primary product ion (HNO^+) with the reactant molecule [Reaction (4)]. The NO^+ product ion is clearly relatively unreactive with CO_2 as has been demonstrated in a previous SIFT study,¹ although it does undergo an association reaction (producing $\text{NO}^+ \cdot \text{CO}_2$) at somewhat higher pressures and lower temperatures, a reaction which is thought to play an important part in ionic synthesis in the Earth's lower ionosphere.¹⁵ The rate coefficient for Reaction (3) ($1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) is essentially equal to the Langevin theoretical value ($1.13 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) and thus indicates unity probability of reaction during an NH^+/CO_2 collision at this energy.

As a final example of the data obtained in this study, those for the complex fast binary reaction $\text{NH}_2^+ + \text{CH}_3\text{NH}_2$ are presented in Fig. 3. In this case, four ions are generated as primary and/or secondary products, these being H_6CN^+ , H_5CN^+ , H_4CN^+ , and H_3CN^+ . Figure 3(b) nicely indicates that all four ions are indeed primary products and that H_6CN^+ is the "terminating ion" in the sequence, i.e., the other three ions undergo secondary reactions with CH_3NH_2 producing H_6CN^+ which we can confidently designate as protonated methylamine CH_3NH_3^+ . The H_5CN^+ ion is most probably CH_3NH_2^+ , but the nature of the H_4CN^+ is less certain although it is most probably CH_2NH_2^+ (rather than CH_3NH^+).¹⁶ The reaction proceeds thus:



Clearly, this is a complicated reaction with product channels which could be considered as resulting from charge transfer (5a), proton transfer (5b), dissociative

charge transfer or hydride ion transfer depending on the neutral product (5c), and H-atom abstraction (5d). That Reaction (5d) is a product channel demands a close interaction and rearrangement and again implies that Reactions (5a), (5b), and (5c) are just three possible decomposition channels for a close encounter, short-lived complex.

Before discussing other specific reactions and the general features of the complete data array, several comments concerning the contents and layout of Table I are necessary. The ions heading the columns are arranged from left to right in order of increasing degree of hydrogenation which also corresponds to increasing proton detachment energy and decreasing recombination energy (these parameters for each ion are also given in Table I—see the caption). The reactant molecules are arranged in order of increasing ionization energy and the proton affinity of each molecule is also given. All but one (i.e., $\text{N}^+ + \text{NO}$) of the N^+ ion reactions were studied previously¹ and are included in Table I for the purpose of comparison. The NH_4^+ data are not presented as part of the table since this ion is unreactive with most of the molecules (see Sec. IV for further comments). The binary rate coefficient determined at 300 K for each reaction is given below the corresponding product ion distribution (in percent), and the Langevin or ADO theoretical rate coefficients^{17,18} are given in the square brackets below the experimental values. In cases where the reaction products are not given, these could not be identified with confidence due mainly to a very slow primary reaction followed by rapid secondary reactions. In only the $\text{NH}_2^+ + \text{CO}$ reaction was an association product observed, and this is assumed to result from a three-body or ternary reaction involving the helium carrier gas (as is included in the particular box in Table I). The rate coefficients quoted are the effective binary rate coefficients at the helium pressures indicated. For the $\text{N}^+ + \text{N}_2$ association reaction, the ternary rate coefficient (in units of $\text{cm}^6 \text{s}^{-1}$) was determined in our previous study.¹ The experimentally determined rate coefficients are considered to be accurate to $\pm 20\%$ for the permanent gases and $\pm 30\%$ for the H_2O , CH_3OH , and H_2CO . Where an approximate (\sim) sign is used, it is intended to indicate an accuracy on the figure of about a factor of 2.

IV. DISCUSSION

It is inappropriate to discuss each of the many reactions given in Table I and we thus restrict ourselves firstly to some general observations of the complete data array, secondly to general comments concerning the reactions of each ionic species, and finally to comment on several of the more interesting reactions of specific reactant molecules.

A. General observations

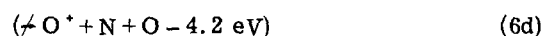
Several general features are apparent in the data array in Table I. For the reactions between the most energetic ions (N^+ and NH^+) and the polyatomic molecules, especially those of low ionization energy and high proton affinity (e.g., CH_3NH_2 , CH_3OH), many exoergic product channels are possible and indeed many but no means all

of these product channels are actually observed. Conversely, as expected, fewer product channels are observed for reactions involving the low recombination energy ions especially for those with the simpler (diatomic) reactant molecules. While most of the reactions proceed at the collisional limit or at appreciable fractions of it, there appears to be a tendency for the reactivity of the ions to decrease somewhat with increasing hydrogenation and thus with reducing recombination energy. This is presumably both a reflection of the particular reaction mechanisms involved in each case (see below) and the fact that fewer energetically allowed binary reaction channels are available, the latter presumably reducing somewhat the probability of a reaction at any given collision.

B. Reactions of the individual primary ion species

1. Reactions of N^+

These reactions have been considered in detail in a previous paper¹ and so will only be alluded to here. The high recombination energy of this ion is conducive to simple charge transfer reactions with all but two of the reactant molecules (H_2 and N_2) and, indeed, the charge transfer product is observed in all energetically allowed cases. However, although long-range electron transfer cannot be ruled out as a possible mechanism, for those fractions of the collisions which result in the charge transfer product, it is clear that in many cases the other product channels can only result from a close interaction between the ion and the molecule since new bonding arrangements are created in both the product ions and product molecules (the latter being inferred from the energetics). For example, it can be seen that for the reaction

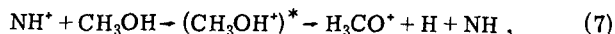


a major product ion is NO^+ [channel (6b)] and NO must be the product neutral (6c) associated with the O^+ product ion, since the dissociative channel (6d) is not allowed energetically. The rate coefficients are generally close to the collisional limit, including that for the CH_3OH reaction ($3.1 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$) for which we previously reported an extraordinarily high value of $4.9 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$,¹ about twice the ADO theoretical value.^{17,18} We have been unable to verify this suspiciously high value and we cannot explain how the error occurred in the previous data. In any event, we now believe that the present, lower value is the more appropriate value for this reaction.

2. Reactions of NH^+

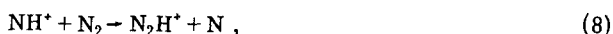
The small proton detachment energy and the relatively high recombination energy of this ion (see Table I) are conducive to simple proton transfer and charge transfer reactions with most of the reactant molecules in Table I. In fact, proton transfer is energetically favorable in all cases, and reaction channels which can be described

as such are observed in all except the NO and H_2S reactions. In view of the high proton affinity of H_2S , it is surprising that H_3S^+ is not observed as a product. Similarly, in all of the reactions in which charge transfer is energetically favorable, such a product channel is observed except for CH_4 and CH_3OH . However, in the $\text{NH}^+ + \text{CH}_3\text{OH}$ reaction, the major product ion is H_3CO^+ and so the reaction may effectively involve dissociative charge transfer:

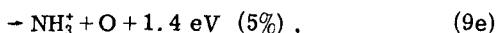
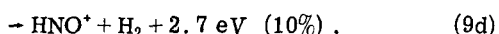
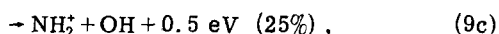
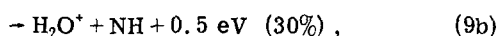
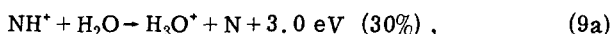


which is exoergic by about 1.4 eV.

Multiple products channels almost invariably result from the interactions; in only one case is a single product ion observed, i.e.,



since in this case no other exoergic channels are available. Ostensibly, simple proton transfer is the reaction mechanism, but even here it is possible that scrambling of the N atoms occurs. This could be checked using the isotopically labeled species $^{15}\text{NH}^+$. The H_2O reaction is perhaps the most complex in that all but one of the energetically allowed product channels are observed, viz.,



This reaction typifies the behavior of this most reactive ion. The rate coefficients are invariably close to the collisional limit and a large fraction of the energetically possible product channels are observed in which almost all possible bonding arrangements have been forged. This can only be the result of a close coupled ion-molecule encounter. There have been few previous studies of NH^+ ion reactions. The rate coefficients for the H_2 and N_2 reactions have been obtained in a flowing after-glow¹² and those for the H_2 and NH_3 reactions in an ICR,^{16,19} which to within the quoted errors are in acceptable agreement with the present data.

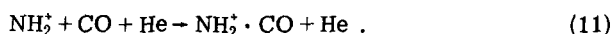
3. Reactions of NH_2^+

This is also a very reactive ion. In general, the rate coefficients are again at or near to the collisional limit. The recombination energy is smaller and the proton detachment energy larger than that for NH^+ and, while this does not significantly affect the rates of the reactions, it does mean of course that fewer reaction channels are energetically allowed, as is manifested in the significantly fewer product channels observed. Although the greater proton detachment energy means that proton transfer reactions can occur with fewer of the molecules, in fact, for every reaction in which this is energetically possible, it is a significant reaction channel. In this respect, the $\text{NH}_2^+ + \text{CO}$ reaction is interesting.

According to the published data,¹⁸ the proton detachment energy of NH_2^+ and the proton affinity of CO are closely equal, i.e., the reaction

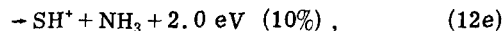
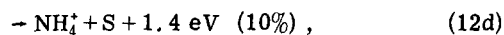
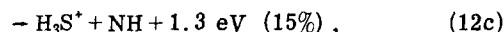
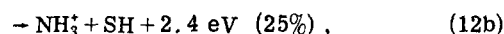
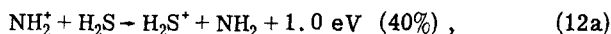


is essentially thermoneutral. Since Reaction (10) is not seen to occur, it strongly suggests that the proton detachment energy of NH_2^+ is significantly greater than the proton affinity of CO. Reaction (10) is of further interest since it proceeds only via the association of the reactants



Although by implication Reaction (11) is a collisionally stabilized association reaction, it did exhibit binary kinetics, i.e., the reaction rate coefficient was independent of the helium carrier gas pressure in our experiment over the range 0.22 to 0.52 torr. It is perhaps significant that NH_2^+ is isoelectronic with CH_3^+ , which our previous detailed studies have shown to exhibit a great propensity to undergo rapid association reactions with several molecular species including CO molecules.²⁰

Most of the various reaction types exhibited in the NH_2^+ reactions are apparent in the H_2S reaction:



including charge transfer (12a), proton transfer (12c), and one- and two-hydrogen-atom abstraction producing NH_3^+ and NH_4^+ ions, respectively.

A few previous observations of the reactions of NH_2^+ ions have been made notably in ICR experiments.^{13,19,21-23} Significant discrepancies are apparent between the ICR data and the present SIFT data especially in the product ion distributions. For example, only two ion products were previously reported²³ for Reaction (12) (H_2S^+ and H_3S^+), although the inevitable presence of NH_3 in the ICR cell and hence the inevitable presence of NH_3^+ and NH_4^+ from ionic reactions with the NH_3 would make it difficult to identify NH_3^+ and NH_4^+ as products of the $\text{NH}_2^+ + \text{H}_2\text{S}$ reaction. This unusually large discrepancy between the ICR and SIFT data illustrates the great difficulties encountered in studying the reactions of these ions in the presence of their parent gas. Perhaps the most surprising discrepancy is that no reaction was observed between NH_2^+ and CH_4 in the ICR,²² whereas it reacts at a near gas kinetic rate in the SIFT (see Table I).

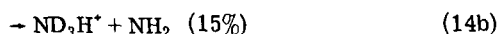
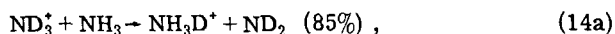
4. NH_3^+ reactions

The low recombination energy and high proton detachment energy of this ionic species renders it unreactive with half of the molecules (see Table I). Charge transfer is energetically possible only with CH_3NH_2 and NO and is very efficient in both cases. Also, proton trans-

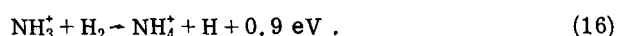
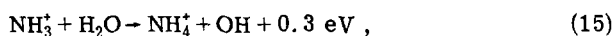
fer is only possible to CH_3NH_2 and NH_3 and it also occurs in both cases. Clearly, the reaction



can be viewed as either proton transfer from the NH_3^+ to the NH_3 or H-atom abstraction from the NH_3 by the NH_3^+ . However, the following indirect evidence points towards proton transfer as the mechanism: It is known from previous detailed studies that proton transfer almost always occurs at the ADO theoretical rate²⁴ and as can be seen from Table I, Reaction (13) does indeed proceed at the ADO rate. Also, all of the other NH_3^+ reactions which proceed at a measurable rate must do so via H-atom abstraction producing the NH_4^+ and, significantly, their rate coefficients are almost always noticeably smaller than their ADO rates, unlike the corresponding N^+ , NH^+ , and NH_2^+ reactions, which we have already stressed in the previous sections proceed largely by charge transfer and proton transfer. We have positively verified that the proton transfer mechanism is indeed operative in Reaction (13) by isotopically labeling the reactant ion. Thus, by using ammonia- d_3 in the ion source, the reaction



was observed to be clearly in favor of the deuteron transfer channel (14a) although not to the total exclusion of the H-atom extraction channel (14b). Thus, it appears—albeit from a limited amount of data—that exoergic H-atom abstraction generally occurs with less than unity probability at an ion-molecule collision at thermal energy. Extreme examples of this principle are the reactions



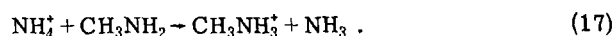
Reaction (15) proceeds at only about 1% efficiency and Reaction (16) is practically immeasurable (see Table I for estimates of the rate coefficients). In the complete data array, there are several reactions which support this general principle. There is, however, one glaring exception: the $\text{NH}^+ + \text{H}_2$ reaction in which the H-atom abstraction channel is greatly favored over the proton transfer channel [note that the latter reaction channel is barely exoergic (~ 0.1 eV)] and the reaction proceeds at close to the gas kinetic rate. In this case, the exception apparently defies the rule! However, it is worth reiterating that the terms proton transfer and H-atom abstraction are used to describe the individual product channels and their use is not intended to imply that the interaction is an especially simple one. Other factors, such as the availability of intermediate energy states and potential surfaces, determine the course of these reactions which involve heavy particle exchange and new bonding arrangements. So the observation discussed above can at best be considered as a useful generality and not a golden rule.

A few of the NH_3^+ reactions have been studied previously in flowing afterglow^{25–28} and ICR^{19,22,23,29} experiments. The rate coefficients obtained are in reasonable

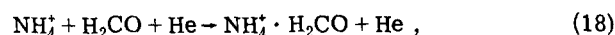
agreement with the present values, but again differences exist between the ICR and SIFT product distributions. For the H_2S reaction, we observe only NH_4^+ as the product ion whereas the ICR experiment²³ indicates the product ions as NH_4^+ (85%), H_3S^+ (15%), and H_2S^+ (<4%). The last two minority product channels are endoergic according to the most up-to-date critical data (Table I), a problem which was recognized and discussed by the previous workers.²³

5. NH_4^+ reactions

This is an extraordinarily stable ion and undergoes few binary reactions. Its high proton detachment energy (= the proton affinity of $\text{NH}_3 = 8.96$ eV) inhibits proton transfer to all the molecules in Table I except CH_3NH_2 , for which it proceeds rapidly:



The rate coefficient obtained is $2.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. It does, however, undergo relatively rapid ternary association reactions with NH_3 , H_2CO , and CH_3OH , e.g.,



which proceed with rate coefficients at 300 K of 10^{-28} to $10^{-27} \text{ cm}^6 \text{ s}^{-1}$. We have not studied any of these association reactions in sufficient detail to be able to quote their rate coefficients confidently. There does exist, however, some flowing afterglow data^{14,30} which support our order-of-magnitude estimates for the ternary association reaction rate coefficients.

C. Reactions of individual molecules

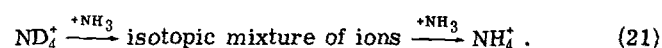
In Sec. IV B above, we showed by the use of isotopic labeling how the $\text{NH}_3^+ + \text{NH}_3$ reaction (14) proceeded largely via proton transfer. It was also apparent from this experiment that no isotopic scrambling occurred during this exoergic reaction, and this was also seen to be the case for the reactions of both ND^+ and ND_2^+ with NH_3 , which both proceeded via parallel charge transfer and proton transfer. So, for example, in the reaction



no NH_2D^+ (equivalent to the charge transfer product NH_3^+) or NH_2D_2^+ (equivalent to the deuteron transfer product NH_3D^+) were observed as primary products. However, secondary reactions of the kind



rapidly ensured that, at the higher NH_3 flow rates, the completely hydrogenated NH_4^+ became the terminating ion. This rapid near-thermoneutral isotopic exchange was clearly demonstrated by injecting ND_4^+ from the ion source and reacting it with NH_3 when successive hydrogenation steps quickly led to the establishment of NH_4^+ ions:



This rapid isotopic exchange between the N–D and N–H bonds has a parallel in the $\text{H}_3\text{O}^+ + \text{D}_2\text{O}$ reaction as we have shown in a recent study.³¹ The reactions of the

ND^+ , ND_2^+ , and ND_3^+ ions with H_2 were similar to the corresponding reactions with NH_3 [e.g., Reaction (19)] in that, for the exoergic reactions



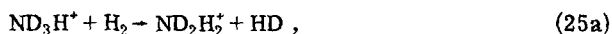
which is the analog of Reaction (2), for



and for



no isotopic scrambling occurred. Also, secondary reactions of the kind



did not proceed at a significant rate. Significantly, however, we find that the reaction



is very rapid. Thus, isotopic exchange in near-thermoneutral reactions between ions and molecules containing like bonds such as N-H and N-D [e.g., Reactions (20) and (21)] and H-H and H-D bonds [e.g., Reaction (26)] is rapid. We have recently observed the same rapid exchange in the reactions of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ions with D_2O .³¹ However, isotopic exchange is very slow between ions and molecules containing unlike bonds such as N-D and H-H bonds [e.g., Reaction (25)] and N-H and O-D bonds (see Ref. 31).

The identity of two of the product ions in the $\text{NH}_2^+ + \text{COS}$ reaction could not be ascertained from the ionic mass only. The product ion at mass 46 amu could have been NS^+ and H_2NCO^+ and that at 48 amu could either be SO^+ or H_2NS^+ . This problem is readily resolved in a SIFT experiment by using ND_2^+ rather than NH_2^+ . In this way, the mass 46 and 48 amu ions were shown to be H_2NCO^+ and H_2NS^+ , respectively.

The very strong bonds in N_2 and CO largely remained intact after the reactions with all of the ions in the sequence, although a small NO^+ product resulted from the $\text{N}^+ + \text{CO}$ reaction. The somewhat weaker bonds in CO_2 and O_2 are much more vulnerable to attack especially in the O_2 case, in which N-O bonds are forged in every reaction at the expense of O-O bonds. The reactions of N^+ and NH^+ with CH_4 result in the formation of ions containing the very strong C-N grouping. The relatively weakly bonded H_2S is greatly fragmented in the reactions, with N-S and H-S bonded ions being evident in the multiple ion products and, significantly, the H_2S reactions proceed at a rate close to the collisional limit (see Table I), which is usual when so many product channels are observed. Such is also evident for the CH_3NH_2 reactions in which multiple products also occur, but for the NO reactions where fewer product channels are available, the rate coefficients are on average somewhat lower than the collisional limit. Clearly, other factors influence the rates of these reactions, such as Franck-Condon overlap in the charge transfer reactions (espe-

cially for the diatomic molecules)³² and so these remarks can only be general observations.

The rate coefficients for the H_2O and CH_3OH reactions are substantially higher (~25%) than their ADO theoretical values (except for the NH_3^+ reactions). Since both these vapors are introduced into the SIFT from prepared mixtures of the vapor in helium (Sec. II), it is quite possible that these mixtures are richer in the vapor than our method of preparation indicated. However, it is unlikely that they are richer by as much as 25%, and we feel that the rate coefficients are most probably somewhat greater than the ADO theoretical predictions. It should be noted that the rate coefficients for the similar molecule H_2CO are close to the ADO value (again except for the NH_3^+ reaction which may be unusual as is discussed in Sec. IV B).

V. CONCLUSIONS

We have presented here a further contribution to the growing body of data relating to thermal energy binary ion-molecule reactions, from which at least the general features of such reactions are being recognized. The present study clearly shows through the detailed product distributions that many of the reactions must proceed via the formation of ion-molecule complexes which survive long enough for considerable bond rearrangement to occur and that the processes of long-range charge transfer and of simple proton transfer are the exceptions rather than the rule in these reactions. However, much too little is known about the details of the reaction mechanisms and in this regard isotopic studies have much to contribute, especially if they can be combined with studies of the energy dependence of the rate coefficients and product ion distributions and with determinations of the energy states of the ionized and neutral products. The imminent addition of a drift tube section to our SIFT apparatus offers the prospect of some such data and if, along with the anticipated increase in useful experimental data, an increased theoretical effort is also forthcoming, then a greater insight into the nature of ion-molecule reactions will surely be obtained. In any event, we hope that this study will stimulate other workers such as ion-beam experimenters to study in detail some of the many and varied reactions which have been studied only superficially here.

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