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Interaction between the ion dipole and the ion-induced dipole in reactions of the polar ion ArH_3^+

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The reactions of the highly polar ion ArH₃⁺ with the nonpolar neutrals Xe, Kr, CH₄, CO, NO, O₂, and N₂ and with the polar neutrals SO₂, H₂O, NH₃, CH₃I, and C₂H₅I have been investigated in a selected ion flow drift tube experiment at near thermal conditions. The rate coefficients obtained have typically 15%-35% larger values than the collisional limiting values k_L and k_{ADO} obtained by the Langevin and ADO (average dipole orientation) theory, respectively. These data are explained on the basis of the interaction between the dipole of ArH₃⁺ and the ion-induced dipole and the permanent dipole, respectively, of the neutral reactants. Rate coefficients for the reactions of H₃⁺ with the above neutrals were also obtained for comparison, as well as the zero field mobility of ArH₃⁺ in helium being (18.5±1.5) cm²/V s. The ion KrD₃⁺ (KrH₃⁺) was detected unambiguously for the first time. Its dissociation energy is larger than 0.29 eV which is the lower limit of the dissociation energy of ArH₃⁺.

INTRODUCTION

Many ion molecule reactions have rate coefficients, k, as large as the collisional limiting value, k_c , i.e., the rate coefficients k_c at which ion-neutral collision complexes are formed are close to the actual rate coefficients observed for these reactions. In the case of the interaction of an ion with a nonpolar molecule, k_c is determined by the ion-induceddipole interaction, and is equal to the Langevin limiting value k_L , which has the temperature independent value¹

$$k_L = 2 \pi e \left(\frac{\alpha}{m_r}\right)^{1/2} \tag{1}$$

being typically $\sim 1 \times 10^{-9}$ cm³ s⁻¹. Here α is the polarizability of the neutral reactant and m_r the reduced mass of the reaction partners. However, when ions react with polar molecules, besides the ion-induced-dipole interaction, the rate coefficients are also influenced by the interaction between the ion and the permanent dipole of the neutral, which yields an additive factor to the Langevin-limiting value, and now the temperature dependent rate coefficient k_{ADO} is predicted by the average dipole orientation (ADO) theory of Su and Bowers²

$$k_{\rm ADO} = \frac{2 \pi e}{m_r^{1/2}} \left[\alpha^{1/2} + C \mu_D \left(\frac{2}{\pi kT} \right)^{1/2} \right], \tag{2}$$

which yields values of k_{ADO} at 300 K being up to twice as high as typical values of k_L , in the case of highly polar neutral reactants. Here μ_D is the permanent dipole moment of the neutral reactant and C a constant, which depends² on the ratio of the dipole moment versus the square root of the polarizability of the neutral reactant $(\mu_D/\alpha^{1/2})$. Recent theories for ion/polar-molecule reactions by Clary³ and Troe⁴ predict more strongly increasing values of k_c at low temperature, but at about 300 K their results closely resemble the ADO predictions. Instead of the ADO values, values of the capture rates $k_{cap}(T)^5$ can also be used for comparing data. These theoretical capture rates were recently obtained by Su and Chesnavich⁵ who performed a parametrization of the ion-polar molecule collision rate constants by trajectory calculations. The values k_{cap} are usually quite close to the ADO predictions.

In much the same way as the permanent dipole of the neutral reactant enhances the collisional limiting value $(k_c = k_{ADO})$ over k_L , one expects that a large dipole of the reactant ion can cause an increase of k_c . Indeed this was shown to happen by Smith et al.⁶ in a selected ion flow tube (SIFT) study of the reactions of ArH₃⁺ at 80 K. Bogey et al.⁷ obtained from microwave spectroscopy the exceptionally large dipole moment for ArH_3^+ of ~9 D and calculations by Hobza et al.⁸ yield $\mu(ArH_3^+) \approx 8$ D in agreement with the result of Bogey et al.⁷ The reactions of ArH₃⁺ with the nonpolar neutrals CH₄, N₂, O₂, and CO (CO has a very small permanent dipole of ~ 0.11 D) showed measured rate coefficients k which exceed the theoretically obtained values k_c by approximately 20%, while at the same temperature the experimental values obtained simultaneously for the reactions of H_3^+ with the neutrals CO, CH₄, and N₂ were equal to k_c to within $\pm 5\%$.⁶

Earlier Rakshit⁹ reported rate coefficients obtained at 300 K for several reactions of ArH_3^+ ions. These measurements together with other ones on reactions of N_2H^+ and H_3^+ were done by Rakshit for test purposes, i.e., checking the capability of a drift tube mass spectrometer system. Several of the results obtained showed strong deviations from respective values reported in the literature by other researchers, but despite that it should be mentioned that most of the rate coefficients for the ArH_3^+ reactions obtained were larger than the collisional limiting values.

The significantly larger values of the rate coefficients of the ArH₃⁺ reactions over k_c were attributed by Smith *et al.*⁶ to the interaction of the dipole moment of the ion with the quadrupole moment of the neutrals. Clary¹⁰ reported an approximate formula for the rate coefficient for the reaction between dipolar and quadrupolar molecules as

$$k = 0.857 \pi \left(\frac{\mu_d Q}{m_r}\right)^{1/2}$$
, (3)

where μ_d and Q are the dipole and quadrupole moments, and m_r is the reduced mass of the reactants. For the reaction of ArH_3^+ with O₂, this formula predicts an increase of k over k_c due to the interaction of the dipole moment of ArH_3^+ with the quadrupole moment of O_2 of 9×10^{-11} cm³ s⁻¹, which is comparable to the measured increase of k above k_c observed by Smith *et al.*⁶ for this reaction, being 1.3×10^{-10} cm³ s⁻¹. It was noted by Smith *et al.*⁶ that CH_4 has no quadrupole moment and yet the measured k exceeded k_c by about 14% which makes it uncertain that the general increase of k for reactions of ArH_3^+ over k_c is due to the ion-dipole/neutralquadrupole interaction. At higher temperatures, such as 300 K reactions of ArH_3^+ ions were not investigated in the experiment of Smith et al.,⁶ as there was not sufficient concentration of these ions in the flow tube. On the other hand, at 80 K reactions with neutrals having permanent dipole moments could not be investigated due to condensation of these neutrals in the SIFT. This was quite unfortunate, in view of Clary's predictions¹⁰ that the increase in the collisional rate coefficient resulting from a dipole/dipole interaction should be about an order of magnitude greater than due to a dipole/ quadrupole interaction.

The investigation of ArH_3^+ reactions with polar molecules therefore provides a crucial test of the interaction causing the increase of the measured rate coefficients over the collisional limiting values k_c . In the present work we report results on these kind of reactions, which were obtained using a selected ion flow drift tube (SIFDT) at 300 K buffer gas temperature. Both polar neutrals SO₂, H₂O, NH₃, CH₃I, C₂H₅I, and nonpolar ones, CO, NO (which are just barely polar), O₂, N₂ having quadrupole moments, and the nonpolar neutrals Xe, Kr, CH₄ with no quadrupole moments were used as reactants. This selection of neutrals was made with the aim of definitely determining which kind of interaction is causing the unusual enhancement of rate coefficients in ArH_3^+ reactions. For comparison, also the reactions of H_3^+ ions with the same neutrals were measured. It should be stressed that this is a vital part of the experiment because the rate coefficients for the reactions of H_3^+ act as reference values, from which accurate values of the ArH₃⁺ reaction rate coefficients can be obtained, thus eliminating systematic measurement errors.6

EXPERIMENT

The SIFDT apparatus used for the present experiment has been described in detail in the literature.¹¹ Thus only those features which are specific for the present investigation are mentioned in the following. Ar_2^+ ions are produced in a high pressure electron impact ion source via the Hornbeck– Molnar process¹²

$$Ar^* + Ar \rightarrow Ar_2^+ + e \tag{4}$$

and three-body association¹³

$$Ar^+ + 2Ar \rightarrow Ar_2^+ + Ar, \tag{5}$$

and then injected into the drift region via a Venturi type injection system.¹¹ H_2 added to the He buffer gas initiates the fast reactions

FIG. 1. Branching ratio of the products ArH^+ and ArH_2^+ from the reaction of Ar_2^+ with H_2 as a function of the mean relative kinetic energy $E_{c.m.}$ between the reactants.

$$Ar_2^+ + H_2 \rightarrow ArH^+ + H + Ar \quad (\sim 80\%) \tag{6a}$$

$$\rightarrow \operatorname{ArH}_{2}^{+} + \operatorname{Ar} \quad (\sim 20\%), \tag{6b}$$

which is in agreement with earlier observations at 300 K of Shul *et al.*¹⁴ and Bedford and Smith,¹⁵ and

$$ArH_2^+ + H_2 \rightarrow ArH_3^+ + H \quad (\sim 10\%)$$
 (7a)

$$\rightarrow H_3^+ + Ar + H \quad (\sim 90\%),$$
 (7b)

which was obtained presently at near 300 K, so that approximately 2% of the initially injected Ar_2^+ ions are converted into ArH_3^+ . Checks were also made on a reaction sequence starting with

$$ArN_2^+ + H_2 \rightarrow ArH^+ + N_2 + H \tag{8a}$$

$$\rightarrow \operatorname{ArH}_2^+ + \operatorname{N}_2,$$
 (8b)

the ArH_2^+ reacting further to produce ArH_3^+ and H_3^+ as shown above, but no higher intensity of ArH_3^+ ions was obtained in this way. H_3^+ is predominately produced by the reaction

$$ArH^+ + H_2 \rightarrow H_3^+ + Ar, \qquad (9)$$

the ArH⁺ being formed in initial reaction (6a). The E/N (where E is the electric field strength and N the buffer gas number density) in the drift section, operated with helium, was kept quite low at values from 5 to 12 Td. At higher E/Nthe ArH₃⁺ ion signal was too small to allow for accurate investigations of rate coefficients. The strong decline of the concentration of ArH₃⁺ with increasing energy is due to the disappearance of the necessary intermediate ArH₂⁺, as is shown in Fig. 1 and presumably in part due to breakup of ArH₃⁺. This is consistent with the observation of Bedford and Smith,¹⁵ that the production of ArH₂⁺ in reaction 6 at 80 K is strongly enhanced over the one at 300 K.

The explanation as to why in the present SIFDT experiment a sufficiently high count rate of ArH_3^+ could be obtained at 300 K but not in the SIFT experiment of Smith

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FIG. 2. Typical set of raw data, from which the rate coefficients for the reactions of H_3^+ and ArH_3^+ , respectively, with SO₂ are obtained.

et al.⁶ most likely lies in the presence of the small drift field in our SIFDT experiment, which causes an enhanced forward motion of the ions, thus reducing the relative importance of lateral diffusive losses. The typical ArH_3^+ ion count rate at the downstream quadrupole mass spectrometer was 30–50 counts/s (with a background of less than 0.05 counts/s), which is quite sufficient to allow for the measurement of rate coefficients of ArH_3^+ reactions with an accuracy of better than $\pm 10\%$ if sufficiently large integration times are used. A typical set of raw data is shown in Fig. 2 where measured count rates for the ions H_3^+ , ArH_3^+ , and SO_2H^+ as a function of the reactant gas flow of SO_2 are presented. The reactions of H_3^+ and ArH_3^+ were measured simultaneously, thus yielding quite accurate ratios of the rate coefficients $k(H_3^+)/k(ArH_3^+)$. It is well known,⁶ that H_3^+ undergoes proton transfer with the above-mentioned neutrals at the Langevin or ADO limiting rate. This fact together with the precise values of $k(H_3^+)/k(ArH_3^+)$ obtained allows one to obtain quite accurate comparisons of $k(ArH_3^+)$ with the corresponding Langevin or ADO-rate coefficients.

The calculation of the rate coefficients from the decline of the primary ion signal when reactant gas was added at an inlet port in the reaction region was done in the way as described by McFarland *et al.*¹⁶

RESULTS AND DISCUSSION

The mobility of ArH₃⁺ in helium was measured to be $\mu_0 = (18.5 \pm 1.5) \text{ cm}^2/\text{V}$ s at E/N = 5 and 12 Td using the technique described by McFarland *et al.*¹⁶ This value at such low E/N can be regarded as being close or equal to the zero-field mobility of ArH₃⁺, which is somewhat lower than the zero-field mobility of Ar⁺($\mu_0 = 20.5 \pm 1.6 \text{ cm}^2/\text{V}$ s) and the one of ArH⁺($\mu_0 = 19.4 \pm 1.6 \text{ cm}^2/\text{V}$ s). Also for mobilities of various other ions of the type XH_u⁺(u = 1,2,...), where X is a neutral, like O₂, C, and N^{17,18} it was observed that with the growing number *u*, the mobilities decrease by approximately one mobility unit at each addition of an H atom. At higher E/N the mobility of ArH₃⁺ could not be obtained due to insufficient ArH₃⁺ ion signal.

The results obtained in the present study for the rate coefficients for the reactions of ArH_3^+ together with results for the H_3^+ reactions with the same neutrals are summarized in Table I. All the rate coefficients were measured several times and the values of the rate coefficients listed in Table I are averaged values. For comparison in Table I we used the theoretical ADO values² rather than the capture rates k_{cap} ,⁵ because of their better agreement with the measured rate coefficients in the case of H_3^+ reactions, which were measured simultaneously. The typical scatter of the data is seen from

	ArH3 ⁺					H3 ⁺					
Reactant	k (300K) this work	kc	k/k _c (300K)	k/k _c other (80K)	Product	α[Å ³]	μ[D]	k (300K) this work	k _c	k/k _c	Product
NO	1.02	0.77	1.32		NOH ⁺	1.70	0.15	1.94	1.95	0.99	NOH ⁺
N_2	0.90	0.75	1.17	1.27 Ref.6	N_2H^+	1.74	0	1.74	1.89	0.92	N_2H^+
CO	1.02	0.82	1.24	1.16 Ref.6	COH ⁺	1.95	0.11	2.03	2.03	1.00	COH ⁺
CH ₄	1.24	1.10	1.13	1.14 Ref.6	CH5 ⁺	2.59	0	2.40	2.35	1.02	CH_5^+
Kr	0.85	0.69	1.17		KrH ₃ ⁺	2.48	0	1.04	2.17	0.48	KrH ⁺
Xe	1.15	0.83	1.33		XeH ⁺ ?	4.04	0	2.49	2.75	0.91	XeH ⁺
		<u> </u>	1.02		76113					0.07	
L			1.23	1.19		<u> </u>				0,97	
H ₂ O	2.50	2.01	1.24		H_3O^+	1.45	1.85	4.81	4.50	1.07	H ₃ O ⁺
NH ₃	2.56	1.88	1.36		NH4 ⁺	2.26	1.47	4.39	4.14	1.06	NH_4^+
SO ₂	2.00	1.50	1.33		SO_2H^+	3.72	1.63	4.93	4.48	1.10	SO_2H^+
CH ₃ I	2.13	1.61	1.33		CH ₄ I ⁺	7.97	1.62	5.39	5.36	1.01	CH_4I^+
C_2H_5I	2.25	1.80	1.25		$C_2H_6I^+$	10.0	1.91	5.86	6.10	0.96	$C_2H_6I^+$
			1.30							1.04	
02	0.60	0.68	0.88	1.18 Ref.6	ArO ₂ H ⁺	1.58	0	0.65	1.79	0.36	$O_2 H^+$
D ₂	0.42	1.09	0.38		ArH ₂ D ⁺	0.79	0	0.58	1.59	0.36	H_2D^+
				ļ	ArD_2H^+						D_2H^+

TABLE I, Rate coefficients in units of 10^{-9} cm³ s⁻¹ for the reactions of ArH₃⁺ and H₃⁺ with the nonpolar gases NO, N₂, CO, CH₄, Kr and Xe as well as O₂ and D₂ and the polar ones H₂O, NH₃, SO₂, CH₃I, and C₂H₅I.

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FIG. 3. Rate coefficient for the reaction of ArH₃⁺ with O₂ as a function of the mean relative kinetic energy, $KE_{c.m.}$, between the reactants. The value of Smith *et al.* was taken from Ref. 6.

Figs. 3 and 4, representing results for the reactions of ArH_3^+ with O_2 and D_2 , respectively. In the case of H_3^+ , in accordance with earlier results,⁶ only proton transfer reactions are observed, and also in the case of ArH_3^+ proton transfer seems to be the dominant reaction mechanism, except where this is not possible due to energetic reasons, as in the reaction with O_2 ,⁶ where the product ArO_2H^+ is observed and in the reaction with Kr, where a simple switching reaction occurs. The binding energy of Kr to H_3^+ is larger than that for Ar to H_3^+ (see Hobza *et al.*,⁸ Fig. 2). Thus switching is exoergic, and occurs at the collisional rate, while proton transfer is endo-ergic (see below). Using the reaction

$$ArD_3^+ + Kr \rightarrow KrD_3^+ + Ar, \tag{10}$$

we could clearly identify KrD_3^+ as the ionic product, which is to our knowledge the first observation of this ion and which confirms that KrH_3^+ is more strongly bound than ArH_3^+ .⁸ A recent experimental value for the dissociation energy of ArH_3^+ of (0.33±0.04) eV is reported by Bedford *et al.*,¹⁵ therefore a lower limit for the dissociation energy of KrH_3^+ is 0.29 eV. A typical set of data for the reactions of D_3^+ and



FIG. 4. Rate coefficient for the reaction of ArH_3^+ with D_2 as a function of the mean relative kinetic energy, $KE_{c.m.}$, between the reactants.



FIG. 5. Typical count rates of ions involved in the reactions of D_3^+ and ArD_3^+ , respectively, with Kr, as a function of the Kr-reactant gas flow.

 ArD_3^+ , respectively, with Kr is shown in Fig. 5. While the reaction of D_3^+ with Kr proceeds via proton transfer,

$$D_3^+ + Kr \rightarrow Kr D^+ + D_2, \tag{11}$$

 ArD_3^+ performs a switching reaction as in Eq. (10).

The ratio of the product ions ${}^{84}\text{KrD}^+/{}^{86}\text{KrD}^+$ $\approx {}^{84}\text{KrD}_3^+/{}^{86}\text{KrD}_3^+\approx 3.5$ closely resembles the ratio of the contents of the most abundant isotopes ${}^{84}\text{Kr}$ and ${}^{86}\text{Kr}$ in natural krypton, being 56% and 16%, respectively. Unfortunately we could not perform the same test with Xe. Because of its larger mass it falls into another mass range of our mass spectrometer, which is less sensitive and therefore the small count rates do not allow for a positive separation between the various XeH⁺(XeD⁺) and XeH_3^+(XeD_3^+) isotopes.

In the case of ArH_3^+ reacting with O_2 , proton transfer and presumably the switching into $O_2H_3^+$ is endoergic. The observed product ArO_2H^+ cannot be regarded as a simple *switching product*, because in this case, the H_3^+ ion breaks up and new bonds are formed. This rearrangement of bonds requires more time than a simple switching or proton transfer. Therefore a negative energy dependence (or temperature dependence) is expected for this reaction. This agrees with the observation that the rate coefficient for this reaction under our conditions (slightly above thermal) is somewhat smaller than at 80 K, as observed by Smith *et al.*⁶

Comparison of the rate coefficients with the collisional limiting values, or capture rates, k_L and k_{ADO} , respectively, which are also included in Table I, shows quite distinct features. In the case of the reactions of H_3^+ ions there is quite good agreement between the measured rate coefficients and the calculated capture rates to within $\pm 10\%$ in all cases, with the exception of O₂ and Kr. For reactions, where $k \cong k_c$, the measured values k generally agree well with values reported in the literature. In view of the large number of such reported

values, we did not include them in Table I. The rate coefficient for O_2 is smaller than k_L , reflecting the slight endoergicity of the proton transfer

$$H_3^+ + O_2 \rightarrow O_2 H^+ + H_2 - 0.33$$
 kcal/mol (Ref. 19). (12)

The presently obtained value $k_{12}=6.5\times10^{-10}$ cm³ s⁻¹ agrees well with the one reported by Smith *et al.*,⁶ $k_{12}=7\times10^{-10}$ cm³ s⁻¹. The nearly thermoneutral proton transfer

$$H_3^+ + Kr \rightarrow KrH^+ + H_2 + 0.3$$
 kcal/mol (Ref. 20). (13)

most likely is influenced by an entropy change of the reaction. The present value $k_{13}=1.04\times10^{-9}$ cm³ s⁻¹ agrees well with the one ($k_{13}=1.1\times10^{-9}$ cm³ s⁻¹) reported by Bohme *et al.*²¹

All the rate coefficients measured for ArH₃⁺ ions exceed the capture rates by typically 23% (ranging form 15% to 36%) with the exceptions of O_2 and D_2 . Within the group of nonpolar molecules there is no distinct difference in the enhancement of the rate coefficients between the neutrals having quadrupole moments (CO, NO, O₂, N₂), and the ones without (Kr, Xe, CH₄), this enhancement being on the average 23% of the respective Langevin rate coefficients (see also Rebrion *et al.*).²² The enhancement of the rate coefficients of ArH₃⁺ reactions with polar molecules over the ADO-limiting values, k_{ADO} , seems to be somewhat higher, averaging about 30%. These results suggest the following interpretation. The enhanced rate coefficients of the reactions of ArH_3^+ with nonpolar neutrals both with and without quadrupole moments, $k > k_c$, reflect the additional interaction between the ion dipole and the ion-induced dipole on the neutrals. It is the force acting between the charge of the ion and the induced dipole of the neutral which governs the value of k_L and thus an additional permanent dipole of the ion causes an additional force due to the ion-dipole/ion-inducedneutral-dipole interaction, yielding a "modified Langevin value" k_{L,ID}

$$k_{L,\mathrm{ID}} = 2 \pi e \left(\frac{\alpha}{m_r}\right)^{1/2} + f(\mathrm{ID}/\mathrm{IND-D}), \qquad (14)$$

where f(ID/IND-D) is an additive factor dependent on a relation between the ion-dipole and the ion-induced-neutraldipole. Additional support for this explanation is provided by the data of the ArH_3^+ -polar neutral reactions included in Table I. If we regard the average of the ratios $k/k_{\text{ADO}} \approx 1.30$ for these reactions to be significantly larger than the ratios $k/k_L \approx 1.23$ for the reactions with nonpolar neutrals, this may show the additional interaction between the ion-dipole and the neutral-permanent dipole, causing an additive factor to the ion-dipole/induced-dipole interaction. The data in Table I show a general increase of the difference $k - k_c$, which represents the absolute enhancement, of the measured rate coefficients k of reactions of ArH_3^+ over k_c with growing polarizability of the neutrals. However, this is not a simple linear correlation as the data show.

In order to obtain a first order theoretical prediction of $k_{L,\text{ID}}$ and thus of the influence of the permanent dipole of ArH_3^+ on its reactivity with nonpolar neutrals, we extended the common Langevin model as shown in the following. The Langevin model is based on an effective potential²³



FIG. 6. Energy dependence of the calculated ratio $k_{L,\text{ID}}/k_L$ for the reaction of ArH₃⁺ with CH₄ (solid symbol represents the present result, the open symbol represents the result of Ref. 6).

$$V_{\rm eff} = \frac{bE}{R^2} - \frac{\alpha e^2}{2R^4} \,. \tag{15}$$

Here, b is the impact parameter, E the collision energy, e the charge of the ion, and α the averaged polarizability of the neutral. This effective potential has a maximum and if we assume that all collisions having enough energy to surmount the barrier indeed lead to chemical reactions, we get a maximum impact parameter b_{\max} , which allows one to calculate the capture rate coefficient called Langevin rate coefficient, k_L , which is independent of collision energy,

$$k_L = \langle v b_{\max}^2 \pi \rangle = 2 \pi \left(\frac{\alpha}{m_r}\right)^{1/2}, \tag{16}$$

where m_r is the reduced mass of the reactants. A permanent dipole on the ion induces a dipole in the neutral reactant giving rise to an additional term in the effective potential, which is then²⁴

$$V_{\rm eff} = \frac{bE}{R^2} - \frac{\alpha e^2}{2R^4} - \frac{\mu_i^2 \alpha}{R^6} \,. \tag{17}$$

Here μ_i is the permanent dipole moment of the ion. The inclusion of the dipole-induced dipole term $-C_6/R^6$ increases the theoretical thermal energy capture rate coefficient $k_{L,\text{ID}}$ slightly above k_L and shows, interestingly, growing values $k_{L,\text{ID}}$, with increasing collision energy (Fig. 6). This was already suggested by Su and Bowers²³ and is in agreement with Clary²⁵ who connects the temperature dependence of the classical capture rate coefficient with the power *n* of the included interaction term which results in a $T^{(1/2-2/n)} = T^{1/6}$ temperature dependence of the rate coefficient if the dipole-induced dipole term is used.

Figure 7 shows the ratio $k_{L,ID}/k_L$ for the case of ArH₃⁺, as a function of the polarizability α of the neutral collision partner. Also included are the measured ratios k/k_c (k_c being k_L and k_{ADO} , respectively) for the reactions of ArH₃⁺ with the neutrals indicated in the Fig. 7. Surely more theoretical work on this subject is required in order to obtain more in-



FIG. 7. Calculated ratio $k_{L,\rm ID}/k_L$ as a function of the polarizability α , for ArH₃⁺ reactions and respective data obtained for ArH₃⁺ reactions with non-polar (solid symbols) and polar (open symbols) neutrals.

sight into the quantitative effects of ion-dipole/induceddipole and permanent-dipole interaction, respectively.

CONCLUSION

The present data, showing rate coefficients for ArH_3^+ reactions which are distinctively larger than the calculated collisional limiting values, k_L and k_{ADO} respectively, are explained on the basis of an additive force acting due to the ion-dipole/ion-induced dipole interaction. The present data and the ones in Ref. 6 are probably accurate enough to act as test cases for theoretical calculations on this subject. An extension of the Langevin and ADO theory including the ion dipole/ion-induced dipole and neutral permanent dipole interaction, respectively, should yield a quantitative expression to predict rate coefficients for reactions of ions with large permanent dipole moments.

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- ¹G. Gioumousis and D. P. Stevenson, J. Chem. Phys. 29, 294 (1958).
- ²T. Su and M. T. Bowers, Int. J. Mass Spectrom. Ion Phys. 12, 347 (1973).
- ³D. C. Clary, Mol. Phys. **54**, 605 (1985).
- ⁴J. Troe, Chem. Phys. Lett. **122**, 425 (1985).
- ⁵T. Su and W. J. Chesnavich, J. Chem. Phys. 76, 5183 (1982).
- ⁶D. Smith, P. Spanel, and D. Bedford, Chem. Phys. Lett. **191**, 587 (1992).
 ⁷M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes, Phys. Rev. Lett. **58**, 988 (1987).
- ⁸P. Hobza, R. Zahradnik, and D. Smith, Chem. Phys. Lett. 208, 497 (1993).
- ⁹A. B. Rakshit, Int. J. Mass Spectrom. Ion Phys. 41, 185 (1982).
- ¹⁰D. C. Clary, Mol. Phys. 53, 3 (1984).
- ¹¹H. Villinger, F. H. Futrell, A. Saxer, R. Richter, and W. Lindinger, J. Chem. Phys. **80**, 2543 (1986).
- ¹²J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 621 (1951).
- ¹³ J. D. C. Jones, D. G. Lista, D. P. Warning, and N. D. Twiddy, J. Phys. B, Atom. Mol. Phys. **13**, 3247 (1980).
- ¹⁴R. J. Shul, R. Passarella, B. L. Upschulte, R. G. Keesee, and A. W. Castleman, J. Chem. Phys. 86, 4446 (1987).
- ¹⁵D. K. Bedford and D. Smith, Int. J. Mass Spectrom. Ion Proc. 98, 179 (1990).
- ¹⁶ M. McFarland, D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. **59**, 6620 (1973).
- ¹⁷W. Lindinger and D. L. Albritton, J. Chem. Phys. 62, 3517 (1975).
- ¹⁸K. Peska, H. Störi, F. Egger, G. Sejkora, H. Ramler, M. Kriegel, and W. Lindinger, J. Chem. Phys. 77, 5253 (1982).
- ¹⁹N. G. Adams and D. Smith, Chem. Phys. Lett. 105, 604 (1984).
- ²⁰S. G. Lias, J. F. Liebmann, and R. D. Levin, J. Phys. Chem. Ref. Data 13, 695 (1984).
- ²¹D. K. Bohme, G. I. Mackay, and H. I. Schiff, J. Chem. Phys. **73**, 4976 (1980).
- ²²C. Rebrion, J. B. Marquette, B. R. Rowe, N. G. Adams, and D. Smith, Chem. Phys. Lett. **136**, 495 (1987).
- ²³ T. Su and M. T. Bowers, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, (1979), p. 84.
- ²⁴ E. A. Mason and E. W. Mc Daniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988), p. 389.
- ²⁵D. C. Clary, Annu. Rev. Phys. Chem. 41, 61 (1990).