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Dynamics of the Reaction of N^+ with H_2.

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The reaction $N^+(H_2,H)NH^+$ has been investigated by measuring the velocity vector distribution of product ions formed when a collimated, mass analyzed beam of reactant ions impinges on a target gas. In the 2.5-8.1 eV range of initial relative energies, the reaction proceeds by a direct interaction mechanism with predominant forward scattering. The forward scattered NH^+ is more excited internally than would be expected from the spectator stripping model, and the internal excitation markedly decreases as the scattering angle increases. There is evidence that at initial relative energies below 4 eV, the principal product is NH^+ in the $\underline{a}\ ^4\Sigma^-$ state, while at initial relative energies above 6.5 eV, the $X\ ^2\Pi$ state of NH^+ is formed predominantly.

Investigations[1-5] of the energy and angular distributions of the products of the exothermic atom transfer reactions

$$N_2^+ + D_2 \rightarrow N_2D^+ + D \qquad (1)$$

$$Ar^+ + D_2 \rightarrow ArD^+ + D \qquad (2)$$

have shown that over a wide range of initial relative translational energies, these processes occur by a direct or impulsive interaction mechanism in which the products are predominantly scattered in the forward, or small angle region of the relative velocity vector space. Indeed, despite the differences in molecular complexity and thermodynamics of these reactions, the N_2D^+ and ArD^+ velocity vector distributions are very similar. In order to assess the sensitivity of ion-molecule reactive scattering measurements to such properties of a reaction such as exothermicity, it seemed to us appropriate and valuable to investigate the dynamic of a reaction which had energetics significantly different from those of reactions (1) and (2). Accordingly, we report here our measurements of the velocity vector distributions of NH^+ formed by reaction of $N^+(^3P)$ with H_2.

EXPERIMENTAL

The instrument used in this work consists of a magnetic mass spectrometer for preparation of a collimated beam of primary ions of known mass and energy, a scattering cell to contain the target gas, and an ion detection train made up of an electrostatic energy analyzer, a quadrupole mass filter,

and an ion counter. The detector components and the exit aperture of the scattering cell are mounted on a rotatable lid which permits simultaneous angular and energy measurements on the ion products. The major components of the apparatus have been described in detail previously.[3] In all important respects, the constitution and operation of the apparatus and the data acquisition and reduction techniques were the same as we used in earlier work.

The N^+ ions were produced by impact of 50-100 eV electrons on N_2. Examination of N^+ which had been scattered by He showed[6] inelastic features which could be assigned to collision induced electronic transitions of N^+ from its ground state (^3P) to its first excited ^3D state. Some evidence of the presence of N^+ (^5S) was found in an inelastic feature which was best assigned as $N^+(^5S \rightarrow {}^3D)$ for which the transition energy is 5.59 eV. However, the transition $N^+(^3P \rightarrow {}^5S)$ involving ground state N^+ requires only 5.85 eV, and may be at least partly responsible for what we measure as a 5.7 ± 0.1 eV transition. While some $N^+(^5S)$ may have been present, the reactive scattering measurements (vide infra) gave no evidence of the extremely exothermic reactions of this ion. No evidence of other excited states of N^+ was found. Thus, most if not all N^+ in the momentum analyzed beam was in its electronic ground state.

RESULTS

Twelve experiments were performed in which the velocity spectrum of the product ions in the initial direction of the ion beam was measured. In general, these velocity spectra show an intense NH^+ peak with a velocity greater than that of the center of mass, and a second less intense peak at a velocity less than that of the center of mass. The locations and intensities of these peaks are given in Table I.

In two experiments, complete velocity vector distributions were measured, and contour maps giving the specific product intensity in arbitrary units as a function of the speed and the scattering angle in the center of mass coordinate system. Since the qualitative features of both maps were quite similar, only one is shown in Fig. 1. Differential cross sections in the center of mass system were computed from these maps. Although the resolution in the center of mass system is only 40°, it was clear that the differential cross sections are strongly peaked in the forward or small direction, and essentially constant at angles greater than 80°. There is relatively less forward scattering at 5.01 eV than at 3.98 eV relative energy, which indicates that the product angular distributions are broadened at high energies.

DISCUSSION

The reaction

$$N^+ + H_2 \rightarrow NH^+ + H \qquad (3)$$

has apparently been investigated only once before. Using a

flowing afterglow technique, Fehsenfeld, Schmeltekopf, and Ferguson[7] found a rate constant of 0.56×10^{-9} cc/sec at 300°K, which is between two and three times smaller than the value calculated from the Langenin polarization model.[8] In our own work on this reaction, we have observed qualitatively that the cross section is noticeably smaller than those of the $N_2^+(D_2,D)N_2D^+$ and $Ar^+(D_2,D)ArD^+$ reactions, which is consistent with the finding of Fehsenfeld et al.[7] for the thermal rate constant.

The energetics of the N^+-H_2 reaction are rather uncertain. Recently Liu and Verhaegen[9] have discussed the bond energies and term values for CH and NH^+, and reported an LCAO-MO-SCF calculation which gives 3.39 eV as the NH^+ bond energy. This value is very probably close to being correct, but is if anything too small, since it leads to the conclusion that the N^+-H_2 reaction is 0.15 eV endothermic. This is inconsistent with the rate constant measured by Fehsenfeld et al.,[7] which would allow at most 0.05 eV endothermicity. Another estimate[9] of $D(NH^+)$ based on approximate experimental values of the ionization potential and dissociation energy of NH is 3.7 eV, which would make the N^+-H_2 reaction 0.15 eV exothermic. Since the exact value of the bond energy is unknown, we will assume for the purposes of discussion that it is equal to the mean of these two estimates, or 3.55 eV. This leads to a value of zero for ΔE_o^o, which is equal to the approximate upper limit consistent with the measured rate constant. As we show subsequently the velocity vector distribution of NH^+ also is consistent with a near zero value for ΔE_o^o.

The NH^+ ion has several low-lying electronic states which can be reached at the energies involved in these experiments. The locations of these states and the nature their adiabatic dissociation products are indicated by the approximate potential energy curves[9] in Fig. 2. These data allow us to estimate the limits of Q, the change in the relative kinetic energy which can accompany production of each electronic state. We have

$$Q = -\Delta E_o^o - U$$

where U is the internal (vibrational and rotational) excitation of NH^+ in a particular electronic state whose formation from N^+ and H_2 is accompanied by an energy change of ΔE_o^o. The lower limit for U is zero, and the upper limit is the dissociation energy D of the particular electronic state involved. Thus

$$-\Delta E_o^o - D \leq Q \leq -\Delta E_o^o$$

Table II gives the limits of Q for the five accessible bound electronic states of NH^+.

The intensity data given in Table I and the intensity contour map in Fig. 1 show that over the range of initial relative energies from 2.52 to 8.18 eV there is no symmetry in the product distribution about the ±90° line in the barycentric coordinate system. Thus, despite the fact that NH_2^+ is a known stable gaseous ion, the N^+-H_2 reaction proceeds through a collision intermediate which exists for less than a rotational period, at least in this higher energy regime. In this respect it is very much like the CO^+-H_2 reaction,[10] which

also proceeds by a direct interaction, even though H_2CO^+ is a strongly bound ion.

It is also of interest to contrast the $N^+(H_2,H)NH^+$ with the $O_2^+(D_2,D)DO_2^+$ reaction which has been investigated in our laboratory.[11] The latter is an endothermic reaction in which the collision intermediate $D_2O_2^+$ is bound by 4.6 eV with respect to product asymptotic states, and 2.6 eV with respect to asymptotic reactant states. The formation of DO_2^+ proceeds via a long-lived collision complex when the initial relative energy is less than 5 eV, which corresponds to the collision complex having up to 3 eV in excess of the 4.6 eV necessary to dissociate to products. In the N^+-H_2 system at our lowest relative energy the NH_2^+ collision intermediate has only 2.5 eV internal energy in excess of the approximately 6 eV needed to dissociate to NH^+ + H, and yet does not exist for as much as a rotational period. These observations suggest the following tentative hypothesis. The existence of a deep well in the potential energy surface is not a sufficient condition for the occurrence of a long-lived collision complex as the dominant feature of the reaction dynamics. It is apparently necessary for direct interactions such as spectator stripping which have intrinsically large cross sections to be blocked by energy requirements such as those discussed[11] in connection with the $O_2^+(D_2,D)DO_2^+$ reaction.

Having ascertained the direct nature of the interaction which leads to reaction, it is of interest to see how clearly the final relative energy of the products lies to the predictions

of the primitive spectator stripping model. This comparison is made in Fig. 3, where the Q values measured at the intense forward peak are plotted as a function of the initial energy.

It is clear that at all initial relative energies, the experimental Q value is more negative, and hence the products are more internally exicted than the predictions of the spectator stripping model. Once again a resemblance to the CO^+-H_2 reaction is evident, since this reaction also shows Q values more negative than the spectator stripping predictions in the range of initial relative energies from 2 to 5.5 eV. Evidently the features of the potential energy surfaces which arise from the strongly bound NH_2^+ or H_2CO^+ in their equilibrium configurations also influence the coupling between the atoms in the highly distorted configurations which occur in reaction by direct interaction, and more nearly bring about equilibration of energy between internal and translational modes of the products.

While Fig. 3 shows that the experimental values of Q decrease approximately linearly as the initial relative energy increases from 2.5 to 4 eV, a break in the curve occurs from 4 to 6.5 eV. The occurrence of this break at a value of Q of approximately -3.5 eV suggests that this phenomenon is associated with the fact that the $\underline{a}^4\Sigma^-$ state of NH^+ is unstable with respect to dissociation for $Q \leq -3.5$ eV. If $\underline{a}^4\Sigma^-$ were the only state of NH^+ formed at initial relative energies below

6.5 eV, products would be observed only if they received sufficient acceleration to have $Q \geq -3.5$ eV. On the other hand, if the $X^2\Pi$ state of NH^+ were formed exclusively, Q could go as low as -4.48 eV before NH^+ became unstable, assuming that NH^+ dissociates adiabatically. The form of the curve in Fig. 3 suggests that initial relative energies below 6.5 eV, $NH^+(\underline{a}^4\Sigma^-)$ is the principal reaction product, and that between 6.5 eV and 8.1 eV, the $X^2\Pi$ state is formed predominately.

Figure 1, the contour map of scattered intensity, shows that virtually all NH^+ is enclosed by a circle which corresponds to Q = 0.6 eV. This strongly suggests that the maximum Q, and hence $-\Delta E_o^o$, is less than 0.6 eV, since motion of the target gas and finite apparatus resolution generally cause intensity to appear in regions which correspond to Q values greater than the calculated upper limit. Thus the scattering data are consistent with the earlier estimate that $\Delta E_o^o \cong 0$.

In Fig. 1 it is clear that considerable product intensity lies at values of Q less than -3.5 eV, the most negative value at which the $\underline{a}^4\Sigma^-$ state is stable. Some of this intensity may be contributed by any NH^+ which is formed in the $X^2\Pi$ state. However, intensity in this region is by no means proof that $X^2\Pi$ molecules are being formed. It can all be simply explained as a consequence of target gas motion, detector resolution, and primary ion beam width. Similar effects have been found in our investigations of the Ar^+-D_2 and N_2^+-D_2 reactions, where the products do not have low lying excited electronic states.

Figure 1 also shows particularly clearly that the most probable value of Q for the products is a strong function of scattering angle. Small impact parameter collisions which are responsible for large angle scattering lead to NH^+ which has 1.7 eV less internal energy than the NH^+ produced by grazing collisions. Table I shows that this qualitative difference in Q for forward and back scattered products persists over virtually the entire range of initial relative collision energies. Only at the lowest initial relative energy that a back scattered peak can be clearly discerned are the values of Q for forward and back scattered products similar. The increase in Q with increasing scattering angle has also been observed in the N_2^+-D_2 and Ar^+-D_2 systems, although in much less extreme form.

SUMMARY

The reaction $N^+(H_2,H)NH^+$ shows kinematics which are notably different from those of any other ion-molecule reaction studied by the ion beam technique. In the 2.5-8.1 eV range of initial relative energies, the reaction proceeds by a direct interaction mechanism, with predominant forward scattering. No evidence of a persistent collision complex was found, despite the considerable thermodynamic stability of NH_2^+. The total reaction cross section is smaller and the angular distribution is less sharply forward peaked than the product distributions for the N_2^+-D_2 and Ar^+-D_2 reactions. The forward scattered NH^+ is more excited internally than would be expected

from the spectator stripping model, showing that there is some coupling of all atoms even in the higher energy grazing collisions. The product internal energy decreases as the scattering angle increases. The dependence of the most probably internal energy of forward scattered products on the initial relative energy suggests that below 4 eV initial relative energy, the principal product is $NH^+(\underline{a}^4\Sigma^-)$ while above 6.5 eV, the $X^2\Pi$ state of NH^+ predominates. This appears to be the first evidence obtained by scattering techniques of the formation of more than one electronic state of product molecules in a chemical reaction.

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Table I. Energy and Intensity of Forward and Backward Scattering.

E_o	V_o	E_{rel}	$\theta = 0°$		$\theta = 180°$		$\bar{I}_{0°}/\bar{I}_{180°}$
			V/V_o [a]	Q	V/V_o [a]	Q	
20.14	16.7	2.52	(0.923)	(-1.7) [c]	-	-	-
30.09	20.4	3.76	0.923	-2.59	(0.825)	(-2.50)	6
31.84	20.96	3.98	0.927	-2.50	0.820	-2.38	5.3
35.36	22.1	4.42	0.926	-2.83	-	-	-
40.09	23.5	5.01	0.923	-3.43	0.806	-1.73	6.5
45.05	24.9	5.63	0.924	-3.70	0.807	-2.10	4.8
49.80	26.2	6.22	0.929	-3.70	-	-	-
50.09	26.3	6.26	0.932	-3.50	0.805	-2.29	12
53.39	27.1	6.67	0.931	-3.76	0.809	-2.5	7.7
56.61	27.9	7.08	0.932	-4.04	(0.807)	(-2.65)	6.9
60.16	28.8	7.52	0.931	-4.31	0.807	-2.53	4.2
65.41	30.0	8.18	0.934	-4.27	-	-	-

a. Ratio of product velocity at intensity maximum to initial projectile velocity. For the spectator stripping model, $V/V_o = 0.933$.

b. Arbitrary unite.

c. Location of the peak quite uncertain.

Table II

Energies (eV) for NH^+

State	Diss. Products	D^a	$\Delta E_o^{o\,b}$	Q_{min}	Q_{max}
$X\ ^2\Pi$	$N^+(^3P)$, H	4.50	0	-4.50	0
$a\ ^4\Sigma^-$	$N^+(^4S)$, H^+	3.55	0.04	-3.59	-0.04
$A\ ^2\Sigma^-$	$N^+(^3P)$, H	1.83	2.67	-4.50	-2.67
$B\ ^2\Delta$	$N(^2D)$, H^+	2.61	2.81	-5.42	-2.81
$C\ ^2\Sigma^+$	$N^+(^1D)$, H	2.11	4.28	-6.39	-4.28

a. Dissociation energy of state.

b. Energy change of $N^+(H_2,H)NH^+$ reaction for given state.

Figure Captions

Fig. 1. Contour map of the specific intensity of NH^+ plotted in the center of mass coordinate system. The small circles locate the positions of the intensity maxima found in scans of the angular distribution. Formation of the $^4\Sigma^-$ state is forbidden inside the circle marked Q = -3.6 eV. The circle marked Q = 0.6 eV is a reasonable upper limit for the velocity of NH^+ with no internal excitation.

Fig. 2. Qualitative potential energy curves for the low lying states of NH^+. Energies at potential minima and at asymptotes are placed relative to each other according to the experimental data in reference 9 and the assumption of a 3.55 eV dissociation energy for the $^4\Sigma^-$ state.

Fig. 3. The relative kinetic energy change Q for the peak intensity at 0° in the center of mass system plotted as a function of initial laboratory energy of the N^+ projectile. The uncertainty in each value of Q is approximately ± 0.2 eV.

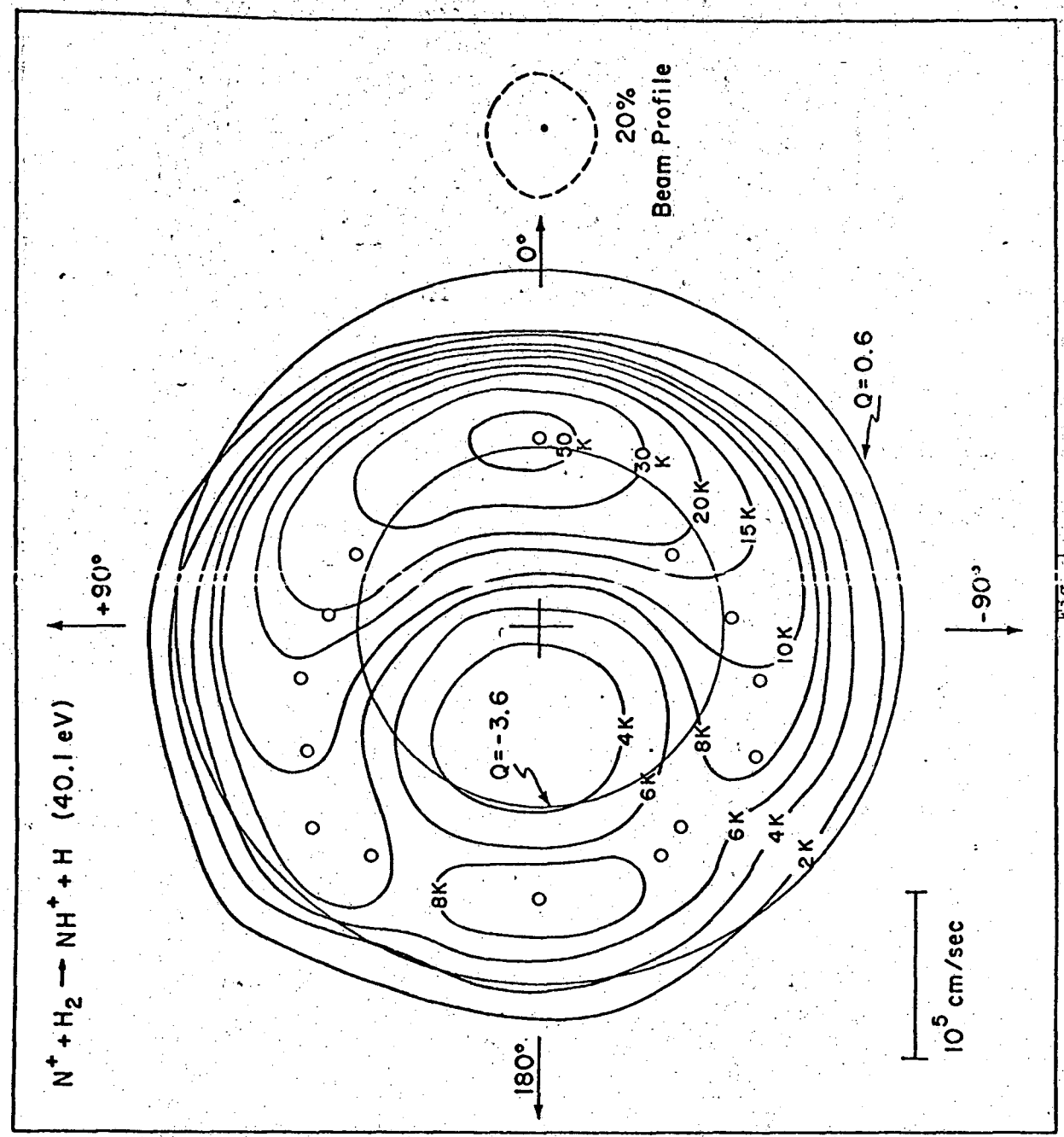
$N^+ + H_2 \rightarrow NH^+ + H$ (40.1 eV)
+90°
0°
-90°
180°
20%
Beam Profile
Q=0.6
Q=-3.6
50 K
30 K
20K
15K
10K
8K
6K
4K
2K
10^5 cm/sec

Fig. 1

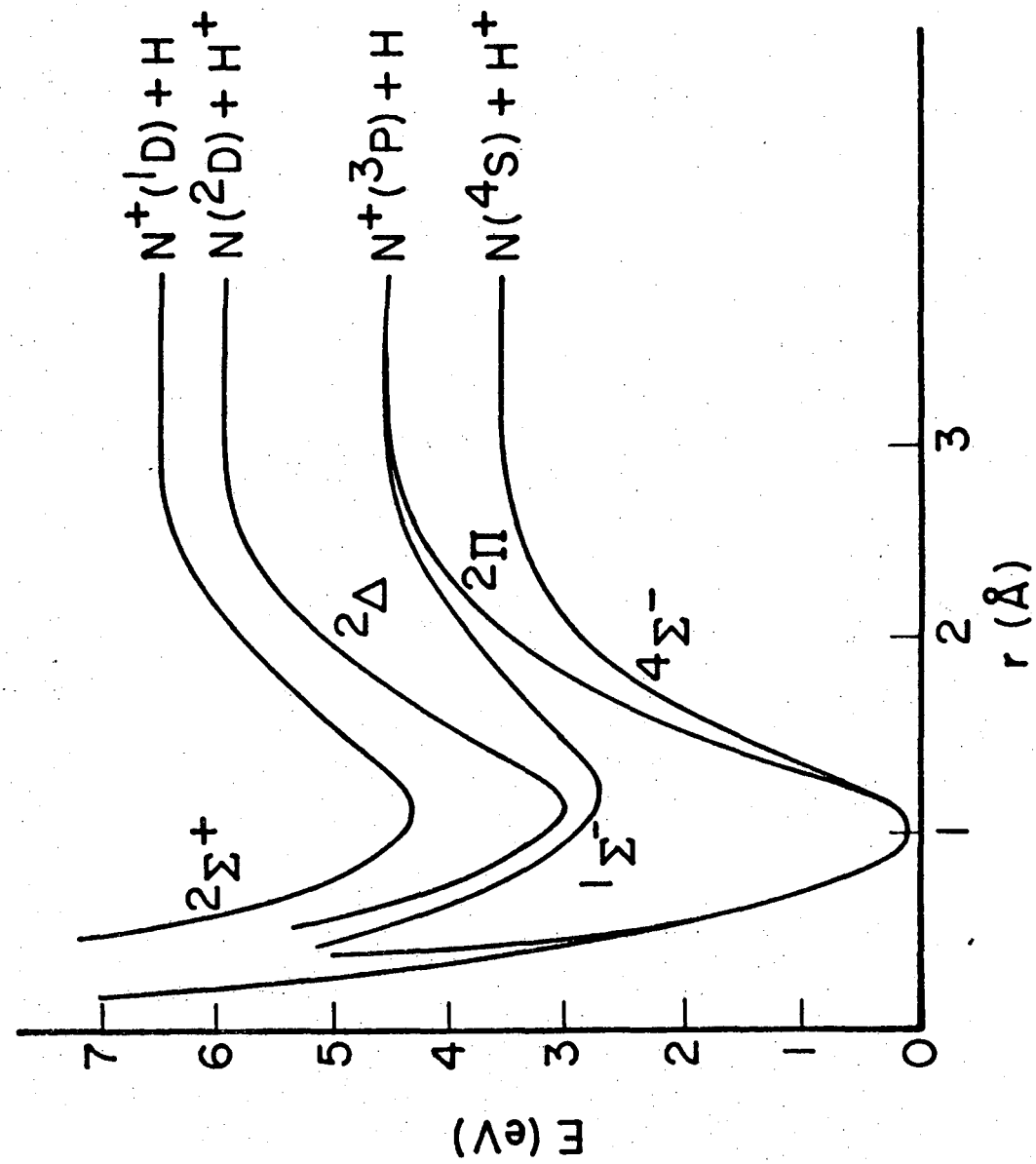
$N^+(^1D) + H$
$N(^2D) + H^+$
$N^+(^3P) + H$
$N(^4S) + H^+$
$^2\Sigma^+$
$^2\Delta$
$^2\Pi$
$^1\Sigma^-$
$^4\Sigma^-$
E (eV)
0
1
2
3
4
5
6
7
r (Å)
1
2
3

Fig. 2

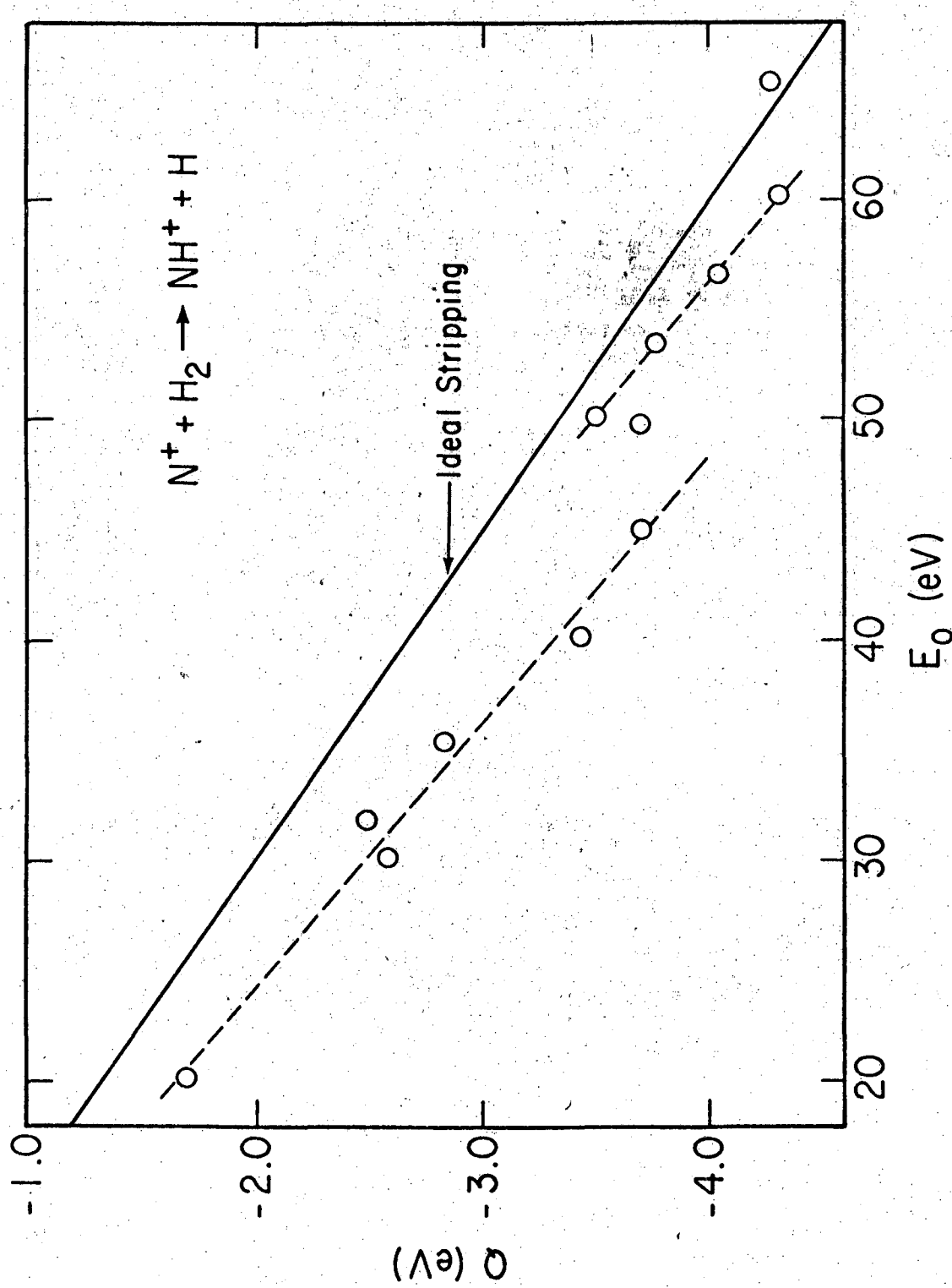

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Fig. 3

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