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# The Dynamics of NeH<sup>+</sup> Production in Ne\*(<sup>3</sup>P<sub>2,0</sub>)-HCl Collisional Autoionization

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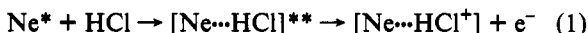
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The ionization of HCl molecules by thermal energy collisions with metastable Ne\* atoms has been studied experimentally and theoretically. The integral elastic cross sections have been measured and analyzed, together with the total ionization cross sections, to obtain an optical potential able to describe the collision dynamics of the neutral reactants. The relative cross sections for NeH<sup>+</sup> and NeD<sup>+</sup> production in Ne\*-HCl or DCl have been measured as a function of the collision energy. A theoretical calculation of the potential energy for the reactive Ne + HCl<sup>+</sup>(A) → NeH<sup>+</sup> + Cl system has been performed by SCF, CI, and CASSCF methods. The dynamics of NeH<sup>+</sup> production is described by two theoretical models. The first one simply couples the semiclassical treatment of Penning ionization with the Langevin criterion for the postionization ion-molecule reaction. The second model also assumes the statistical phase space theory to describe the partitioning of the Ne...HCl<sup>+</sup>(A) ionic complex among the possible final products.

## Introduction

The ionization processes of HCl by collision with neon metastable atoms are relevant for the development of some excimer laser sources. In the XeCl\* laser, for example, the XeCl\* excimer molecules are produced by a discharge in a gaseous mixture of Xe and HCl in an excess of Ne. It has been shown recently that the processes induced by metastable neon atoms, including ionization, play a significant role in the overall mechanism that describes the behavior of the discharge in the laser cavity.<sup>1</sup>

The ionization of HCl by Ne\* in thermal energy collisions is also interesting from a fundamental point of view because it represents a simple atom-molecule collisional autoionization process<sup>2-5</sup> whose dynamics have been successfully described through a two-step mechanism. In the first step an autoionizing collisional complex is formed



Following the ionization step, the collision continues toward the final ionic products

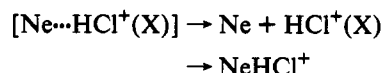


Step 1 provides the initial conditions, such as distributions in energy and angular momentum, for step 2. A recent mass spectrometric study has shown that this autoionization leads to the formation of HCl<sup>+</sup>, NeH<sup>+</sup>, and NeHCl<sup>+</sup> ions.<sup>4</sup> In particular, NeH<sup>+</sup> is the result of a proton-transfer reaction between Ne and HCl<sup>+</sup> after the ionic complex is formed.

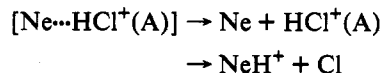
Owing to its interest, the Ne\*-HCl system has been the object of several studies performed with different experimental techniques. The energy analysis of the electrons ejected by the autoionizing collisional complex has shown that two types of ionic complexes can be formed: [Ne...HCl<sup>+</sup>(X)] correlating with ground-state HCl<sup>+</sup>(X) ions and [Ne...HCl<sup>+</sup>(A)] correlating with HCl<sup>+</sup>(A) excited ions.<sup>6</sup> From the electron energy spectrum the nascent vibrational populations of the two electronic states of HCl<sup>+</sup> within the complexes have been obtained. This result also indicates that HCl is only slightly perturbed during ionization, such that the vibrational energy distribution of HCl<sup>+</sup> follows the Franck-Condon principle.

The mass analysis of the produced ions allowed the measurement of the collisional energy dependence of the cross sections for the formation of the three final products that arise from the

dynamical evolution of the ionic complex.<sup>4</sup> In particular from the analysis of the cross sections it has been indicated that while the [Ne...HCl<sup>+</sup>(X)] ground state complex can lead to Penning or associative ions



the excited [Ne...HCl<sup>+</sup>(A)] complex can decompose to HCl<sup>+</sup>(A) or produce NeH<sup>+</sup> through a proton-transfer reaction from HCl<sup>+</sup>(A) to the ground-state neon atom



The HCl<sup>+</sup>(A) ion, once formed, can decay radiatively to the ground state. The spectrum of the emitted photons has been measured, and the vibrational population of this ion at the end of the collision process has been characterized.<sup>7,8</sup>

As recently pointed out, different experimental techniques such as electron and optical spectroscopy or elastic and ionization cross sections are capable of giving information on individual events in the sequence of processes leading to reaction products. Therefore a simultaneous analysis of different experimental data can lead to a rather complete characterization of the microscopic mechanism for the formation of the final product ions. An attempt of this type has been performed in our paper, hereafter referred to as ref 4, using ionization cross sections together with electron spectroscopy data to construct a model that allows the interpretation of the NeH<sup>+</sup> production cross section as a function of the collision energy. The model, which is substantially an adaptation of the "turning point-Langevin" model previously proposed by Siska and co-workers,<sup>5</sup> couples the semiclassical treatment of Penning and associative ionization with the Langevin criterion frequently used in the analysis of ion-molecule reactions. That model gave a good physical description of the collision dynamics leading to NeH<sup>+</sup>. For example, it was clearly shown that the evolution of the [Ne...HCl<sup>+</sup>(A)] complex toward Ne + HCl<sup>+</sup>(A) or NeH<sup>+</sup> + Cl depends on the energy and angular momentum conditions of the complex at the moment of the ionization: these conditions are determined by the collision dynamics between Ne\* and HCl in the entrance channel. However, that model had a particular weakness: owing to the

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lack of experimental information, the interaction potential of the two neutral collision partners was only estimated on the basis of combination rules.

In the present work the problem of  $\text{NeH}^+$  formation in  $\text{Ne}^*-\text{HCl}$  collisional autoionization is revisited in light of new measurements that complement and refine those of ref 4. Moreover the collision dynamics are described with a model that follows the general characteristics of the previous one but includes several improvements. In particular, (a) the  $\text{Ne}^*-\text{HCl}$  integral elastic cross section has been measured as a function of collision energy and the  $\text{Ne}^*-\text{HCl}$  optical potential is obtained by a simultaneous analysis of the integral elastic and the previously measured total ionization cross sections; (b) the branching ratio for  $\text{NeH}^+$  production has been carefully remeasured by using supersonic  $\text{Ne}^*$  beams at different velocities; the branching ratio has been also measured for the ionization of the isotopic  $\text{DCI}$  molecule; (c) the  $\text{NeH}^+$  formation is discussed through a theoretical model using the phase space theory; and (d) a preliminary study of the structure and energy of the  $[\text{Ne}\cdots\text{HCl}]^+(\text{A})$  complex has been performed by CI and CASSCF theoretical calculations.

### Experimental Section

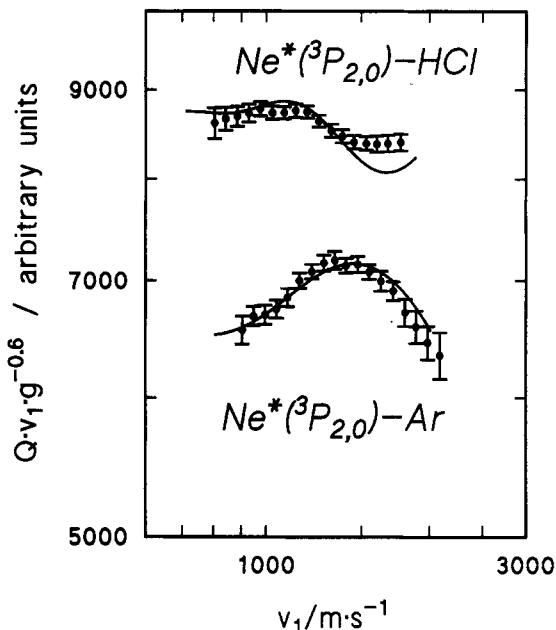
The apparatus used for the present measurements has been described previously in detail.<sup>9,10</sup> Only a brief description is given here. A supersonic or effusive metastable neon atom beam crosses at right angles an effusive beam of  $\text{HCl}$  produced by a glass microcapillary array at room temperature. The  $\text{Ne}^*$  beam is detected by a channel electron multiplier located along the beam path, while the  $\text{HCl}$  beam is monitored by a total ionization detector. The ions produced in the collision zone can be extracted, focused, mass analyzed by a quadrupole filter, and then detected by another channel electron multiplier.

For the measurement of the integral elastic cross sections, a metastable neon beam was produced by electron bombardment of a time of flight velocity selected effusive beam. The cross sections were determined by measuring the attenuation of the metastable neon beam passing through the  $\text{HCl}$  target beam. The collision velocity was analyzed using a time of flight technique: the metastable beam was pulsed by a rotating slotted disk, and the atoms were counted, using a multichannel scaler, as a function of the delay time from the beam opening. Time spectra of the metastable atoms were measured with the detector located about 50 cm from the collision zone. These spectra, measured with the target beam on and off, allowed us to obtain the relative integral elastic cross sections, by using the Lambert-Beer equation, as a function of the collision velocity.<sup>11</sup>

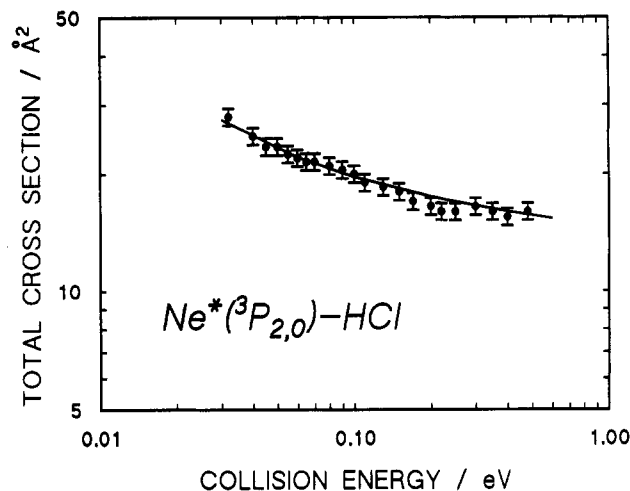
The measurement of the  $\text{NeH}^+$  branching ratio was accomplished by using a supersonic beam at three different nozzle temperatures, each one corresponding to a well defined narrow velocity distribution ( $\sim 10\%$ ). The ions produced in the collision zone, after extraction, were analyzed by a quadrupole mass filter. For each collision energy, mass spectra were recorded leading to the determination of the intensity ratio between the  $\text{NeH}^+$  ions and the total ions produced. To test the best conditions for extraction and acceleration voltages in our experimental arrangement,  $\text{He(I)}$  (58.4 nm) photoionization of molecules whose fragmentation pattern is known was measured using a microwave discharge in pure  $\text{He}$  to produce a UV 58.4-nm photon lamp. The discharge was tuned in order to reduce the production of helium metastable atoms. However the signals produced by photoionization and  $\text{He}^*$  collisional autoionization were separated by time spectra.

### Integral Elastic Cross Sections

The integral elastic cross sections measured as a function of the neon metastable atom velocity are shown in Figure 1. The



**Figure 1.** Integral elastic cross sections for collisions of metastable neon atoms with Ar atoms and  $\text{HCl}$  molecules. The cross sections are plotted multiplied by the metastable atom velocity,  $v_1$ , and the relative velocity  $g^{-0.6}$ , in order to enhance the glory structure. The continuous lines are the cross sections calculated by assuming the potential of ref 12, for  $\text{Ne}^*-\text{Ar}$ , and the present best fit potential, for  $\text{Ne}^*-\text{HCl}$ .



**Figure 2.** Total ionization cross section for  $\text{Ne}^*-\text{HCl}$  collision as a function of the collision energy. The curve is the calculation performed by assuming the present best fit optical potential.

cross sections are multiplied by the neon velocity and the relative velocity  $g^{-0.6}$  in order to enhance the glory structure. The cross sections for  $\text{Ne}^*-\text{HCl}$  are reported together with those measured under the same conditions for  $\text{Ne}^*-\text{Ar}$ , chosen as a test system for the experimental arrangement.

For  $\text{Ne}^*-\text{Ar}$  the continuous line is the result of a theoretical calculation of the cross section performed within the JWKB approximation by using a recent "multiproperty" optical potential obtained in our laboratory.<sup>12</sup> The calculated cross sections have been averaged over the velocity distributions of the two beams and corrected for the finite angular resolution of the experiment. The agreement between the experimental and calculated cross sections is satisfactory.

The  $\text{Ne}^*-\text{HCl}$  cross sections have been analyzed together with the total ionization cross sections previously obtained in our laboratory and shown in Figure 2. From this analysis a spherical optical potential to describe the collision dynamics of  $\text{Ne}^*$  and  $\text{HCl}$  in the entrance channel has been obtained. The analysis has been performed by calculating the integral elastic and total ionization cross sections with an optical potential whose param-

TABLE I: Best Fit Potential Parameters

$\epsilon$	9.67	meV	$\beta'$	5.00	
$R_m$	5.00	Å	$\sigma$	4.422	Å
$C_6$	$2.466 \times 10^5$	meV Å <sup>6</sup>	$R_1$	5.578	Å
$A$	318	meV	$R_2$	9.00	Å
$b$	1.50	Å <sup>-1</sup>	$a_1$	-0.7500	
$\epsilon'$	11.92	meV	$a_2$	1.0234	
$R_m'$	5.13	Å	$a_3$	-2.8878	
$\beta$	6.00		$a_4$	2.3873	

eters have been varied in order to reproduce the experimental cross sections. The potential model used is the following

$$W(R) = V^*(R) - \frac{i}{2}\Gamma(R)$$

where the real part is a Morse-Morse-Spline-van der Waals (MMSV) function

$$V^*(R) = \epsilon' \left\{ \exp \left[ -2\beta' \left( 1 - \frac{R}{R_m'} \right) \right] - 2 \exp \left[ -\beta' \left( 1 - \frac{R}{R_m'} \right) \right] \right\}; \text{ for } R \leq \sigma$$

$$V^*(R) = \epsilon \left\{ \exp \left[ -2\beta \left( 1 - \frac{R}{R_m} \right) \right] - 2 \exp \left[ -\beta \left( 1 - \frac{R}{R_m} \right) \right] \right\}; \text{ for } \sigma < R \leq R_1$$

$$V^*(R) = \alpha_1 + (R - R_1)\{\alpha_2 + (R - R_2)[\alpha_3 + (R - R_1)\alpha_4]\}; \text{ for } R_1 < R < R_2$$

$$V^*(R) = -\frac{C_6}{R^6}; \text{ for } R \geq R_2$$

The imaginary part is given by an exponential model

$$\Gamma(R) = A \exp(-bR)$$

The values of the best fit parameters are reported in Table I. The procedure to obtain these parameters is the following. The  $C_6$  parameter has been fixed to the value calculated by the Slater-Kirkwood approximation as modified by Pirani and co-workers.<sup>13</sup> The  $R_1$  distance has been fixed to the inflection point of the Morse function corresponding to the well region and  $R_2$  to the constant value of 9 Å. The  $\beta'$  parameter has been maintained at the value of 5.0, the value of the Ne\*-Ar system.<sup>12</sup> The  $\epsilon'$  and  $R_m'$  parameters are fixed by the boundary condition at  $R = \sigma$ , with  $\sigma$  the distance where  $V^* = 0$ . The spline parameters are also fixed by the boundary conditions in  $R_1$  and  $R_2$ . In the first step, the  $\epsilon$  and  $R_m$  parameters have been adjusted on the location of the glory maximum along the velocity scale. Taking into account that the interaction between Ne\* and HCl can be described as the sum of a "chemical" contribution to a van der Waals interaction, the van der Waals component has been first estimated on the basis of the combination rules recently suggested by Pirani and co-workers<sup>13</sup> ( $\epsilon \sim 9$  meV;  $R_m = 5.1$  Å). The parameters have then been varied with the constraint that at 5.1 Å the potential has to be  $\leq -9$  meV. In the second step the imaginary part has been adjusted using the total ionization cross section data. Finally the whole optical potential has been refined on both sets of experimental data.

The results of the best fit calculations are shown in Figures 1 and 2. The potential model and the procedure to obtain the potential parameters require some considerations. The model used for the present analysis is spherically symmetric, neglecting the anisotropy of the interaction due to the different orientations of HCl with respect to the incoming metastable atom and the anisotropy arising from the internal spin-orbit structure of the metastable neon. This model leads to an evident overestimate of the calculated glory amplitude<sup>14</sup> compared with the one experimentally observed (see Figure 1). As will be discussed later, the spherical symmetry represents a limitation of the proposed

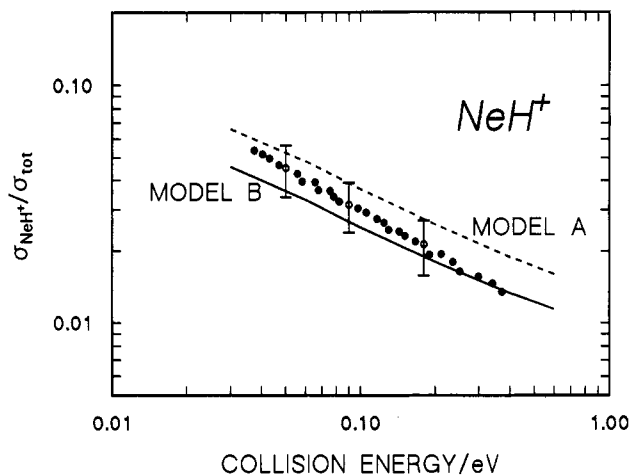


Figure 3. NeH<sup>+</sup> to total cross section ratio as a function of the Ne\*-HCl collision energy. The open circles are the present results, while the full circles are the results of ref 4 normalized to the present ones. The two curves are the calculated cross sections obtained by using the two models proposed in the present work (see text).

TABLE II: Relative Cross Sections for NeH<sup>+</sup> and NeD<sup>+</sup> Production

collision energy, eV	$\sigma(\text{NeH}^+)/\sigma_{\text{tot}}$	$\sigma(\text{NeD}^+)/\sigma_{\text{tot}}$
0.050	$0.076 \pm 0.009$	$0.065 \pm 0.009$
0.090	$0.053 \pm 0.007$	$0.057 \pm 0.007$
0.180	$0.036 \pm 0.005$	$0.034 \pm 0.005$

potential. However, we note the experimental information is insufficient to obtain a significant characterization of the geometric or spin-orbit anisotropy of the interaction. Therefore the present potential must be considered as the best presently available effective potential suitable to describe the gross features of the collision dynamics up to the ionization limit.

### Product Branching

In the previous work of ref 4 the cross sections for the production of HCl<sup>+</sup>, NeH<sup>+</sup>, and NeHCl<sup>+</sup> were measured as a function of the collision energy in the range 0.03–0.4 eV. These cross sections all decrease with increasing collision energy. In particular, the NeH<sup>+</sup> branching ratio ( $\sigma_{\text{NeH}^+}/\sigma_{\text{tot}}$ ) also decreases with increasing energy. That measurement was performed by using effusive beams of neon metastable atoms at room temperature and 800 K, and by selecting the neon metastable velocity with the time of flight technique.

In the present work the branching ratio for NeH<sup>+</sup> production has been carefully remeasured by using a different technique: we employ a supersonic beam of Ne\* at three different nozzle temperatures. Corresponding to each one of these three conditions, an intense beam of neon metastable atoms with narrow velocity distribution ( $\sim 10\%$ ) has been obtained. The advantages of the use of supersonic beams are mainly due to a higher intensity of velocity selected metastable atoms which leads in turn to a higher intensity of product ions for selected collision energies. The branching ratio has been measured for the collision energies of 0.05, 0.09, and 0.18 eV for both Ne\*-HCl and Ne\*-DCl, and the results are reported in Table II. No isotope effect is observed.

The energy dependence of the three measured branching ratios shows excellent agreement with the measurement previously performed using the time of flight velocity selection. However the value of the ratio appears to be slightly lower ( $\sim 25\%$ ) than previously reported.<sup>4</sup> In Figure 3, the measured branching ratio is shown. In the figure, the previously measured branching ratio is shifted toward lower values by a constant factor of approximately 25%. The agreement in the velocity dependence is evident.

The discrepancy of the two measurements must be attributed to the possible error connected with this type of measurement. Problems in the determination of relative abundances of product ions can be present if the ions are formed with different kinetic

**TABLE III: Fragmentation Patterns for He(I) (58.4 nm) Photoionization of CH<sub>3</sub>Cl and CH<sub>3</sub>Br**

	this work	Eland et al. <sup>16</sup>
	CH <sub>3</sub> Cl	
CH <sub>3</sub> Cl <sup>+</sup>	1.00	1.00
CH <sub>2</sub> Cl <sup>+</sup>	0.10	0.06
CH <sub>3</sub> <sup>+</sup>	0.36	0.38
	CH <sub>3</sub> Br	
CH <sub>3</sub> Br <sup>+</sup>	1.00	1.00
CH <sub>2</sub> Br <sup>+</sup>	0.32	0.35
CH <sub>3</sub> <sup>+</sup>	0.43	0.43
Br <sup>+</sup>	0.02	0.02

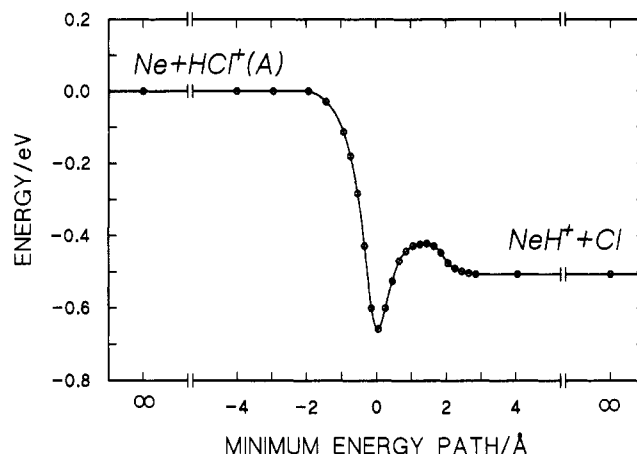
energies or if the quadrupole mass filter operates with mass-dependent transmission.<sup>15</sup> In fact ions at high kinetic energies could easily escape from the collision zone, leading to a collection efficiency lower than expected. This possible error can be minimized when proper conditions for extraction and acceleration voltages are used. In our experiment NeH<sup>+</sup> ions could be formed with kinetic energies higher than HCl<sup>+</sup> due to the exothermicity of the Ne-HCl<sup>+</sup>(A) ion-molecule reaction, 0.42 eV. To check the best conditions for our experimental arrangement, a test has been performed by measuring the fragmentation pattern for He(I) (58.4 nm) photoionization of CH<sub>3</sub>Cl and CH<sub>3</sub>Br. These two systems have been chosen because (a) the He(I) photofragmentation pattern is known;<sup>16</sup> (b) the fragmentation of CH<sub>3</sub>Cl covers a range of masses close to that covered by the ions produced in Ne<sup>\*</sup>-HCl collisions; (c) the dissociative ionization of both molecules leads to the formation of CH<sub>3</sub><sup>+</sup> ions with kinetic energies higher than the parent ions.<sup>16,17</sup>

The results obtained for the photoionization of CH<sub>3</sub>Cl and CH<sub>3</sub>Br are reported in Table III together with those obtained by Eland and co-workers.<sup>16</sup> The good agreement can be considered as an indication of the reliability of the experimental arrangement and conditions employed.

#### Energy and Structure of the [Ne-HCl<sup>+</sup>(A)] Complex

The ionic [Ne...HCl<sup>+</sup>(A)] complex represents the dynamical intermediate between Ne + HCl<sup>+</sup>(A) and NeH<sup>+</sup> + Cl. Its structure and energy are therefore the essential ingredients that determine the proton-transfer dynamics. The knowledge of the potential energy surface (PES) that describes this three-particle reactive system allows a dynamical treatment of the processes. However for this treatment it is necessary to achieve a level of accuracy in the knowledge of the PES often higher than generally obtainable with the usual tools of quantum chemistry. Nevertheless a theoretical calculation of the PES gives good qualitative information that can be of great help for the interpretation of experimental data and, as will be shown later, for the elaboration of a theoretical dynamical model. For this reason energy calculations for this system have been performed by using SCF, CASSCF, and CI schemes at different levels of accuracy. Obviously these calculations do not give an account of the long range forces, mainly ion-induced dipole, but in spite of this limitation some characteristics of the short range regions are also qualitatively reliable.

In a first step the three nuclei Ne-H-Cl have been fixed in a collinear arrangement. The energy calculation has been performed using the GAMESS computer package of M. F. Guest and P. Sherwood. The basis set for Ne comes from the TZVP library of the GAMESS program, taken from ref 18. For chlorine the basis is the (7s5p) contracted set of ref 19 augmented by a d term ( $\alpha = 0.619$ ), and for H the contracted (2s) basis of ref 20, augmented by a polarization p term ( $\alpha = 1.0$ ). In the two CI calculations, approximately 30 000–200 000 configurations were included in the calculation. The calculations explicitly monitor convergence on the excited-state surface correlating with Ne + HCl<sup>+</sup>(A). In this state the HCl<sup>+</sup>(A) ion asymptotically orients its bonding orbital  $\sigma_{1s3p}$ , with one electron, along the direction of the nucleus of neon, while the two filled  $\pi$  orbitals



**Figure 4.** Potential energy profile of the Ne + HCl<sup>+</sup>(A) → NeH<sup>+</sup> + Cl reaction along the minimum energy path as obtained by a SCF-CI calculation for a collinear geometry and in a mass-weighted coordinate representation. Distances are measured from the absolute minimum, which occurs at a Ne-H distance of 1.08 Å and an H-Cl distance of 1.80 Å.

remain orthogonal to that direction. CI calculation yields the behavior of the potential energy along the minimum energy path, and the results are shown in Figure 4. This trend indicates the existence of a weakly bound linear complex and the presence of a barrier in the exit channel toward the NeH<sup>+</sup> + Cl products. In the collinear arrangement this "stable" complex shows bond distances for Ne-H and H-Cl 1.08 and 1.80 Å, respectively.

Although the exothermicity of the reaction is reproduced well by the calculation, it must be considered that the energy values of Figure 4 have only an approximate meaning. Changing the calculation scheme and level of accuracy causes the well depth and height of the barrier to change significantly: with respect to the NeH<sup>+</sup> + Cl asymptote, the well depth can vary from 0.042 to 0.151 eV. Nevertheless all the calculations have always shown the existence of both well and barrier.

In a second step the bond angle has been varied, leaving the Ne-H and H-Cl distances fixed to values close to those corresponding to the minimum of Figure 4. For angles smaller than 170°, the total energy increases rapidly. In conclusion, this qualitative PES characterization indicates that the complex is collinear and weakly bound and that a barrier is present, along the exit channel toward NeH<sup>+</sup> + Cl.

#### Theoretical Model

Before discussing the procedure followed for the calculation of the branching ratio for NeH<sup>+</sup> formation, we recall the key points of the model fully described in ref 4. In that model NeH<sup>+</sup> ions are produced through those collisions which (a) lead to [Ne...HCl<sup>+</sup>(A)] ion complex formation; (b) occur during the approach of Ne<sup>\*</sup> and HCl when the impact parameter is such that, after ionization, Ne and HCl<sup>+</sup>(A) surmount the centrifugal barrier; (c) occur during the separation of the neutral partners when the impact parameter is such that, after ionization, Ne and HCl<sup>+</sup>(A) are "reflected back" by the centrifugal barrier. NeH<sup>+</sup> ions are produced every time Ne and HCl<sup>+</sup>(A) give rise to a "close collision".

A more sophisticated way of approaching the problem of the branching ratio is provided by the microscopic statistical theories of reactions. Among these, the easiest to apply in our case is the phase space theory, which has been already successfully applied to the description of He(<sup>3</sup>S,<sup>1</sup>S)-H<sub>2</sub> collisional autoionization.<sup>5</sup> By this approach, one simply counts the product states accessible for the two channels subject to the constraint of energy and angular momentum conservation. The cross section can be computed by partitioning the cross sections for those complexes formed by close collision among the relative number of states available in each case.

In the following, we analytically describe the main features of these two models. The one where the ion-molecule reaction follows the Langevin criterion is indicated by model A. The modification that introduces the phase space theory gives rise to model B. Model A: The interaction between Ne and HCl<sup>+</sup>(A) is described by an ion-induced dipole potential

$$V_+(R) = -\frac{C_4}{R^4}$$

The condition for Ne-HCl<sup>+</sup> close approach is that the collision impact parameter for the approaching neutral partners is

$$b \leq \frac{1}{R_0(b)} \sqrt{\frac{2C_4}{E}}$$

with  $R_0(b)$  the classical turning point at the collision energy  $E$ . Then the probability of NeH<sup>+</sup> formation is given by the probability that an ionization occurs between  $\infty$  and  $R_0(b)$  for the approaching partners, or between  $R_0(b)$  and  $R_a$  for the separating partners, where  $R_a$  represents the limiting distance given by the equation

$$V^*(R_a) - E - V_+(R_a) + H(b) = 0$$

$H(b)$  is the height of the centrifugal barrier in the Ne-HCl<sup>+</sup>(A) interaction.

Therefore the probability of NeH<sup>+</sup> formation is

$$P_{\text{NeH}^+}(b, E) = f_{\text{HCl}^+(A)} \left( 1 - \int_{R_0}^{\infty} \frac{\Gamma(R) dR}{\hbar v(R, b, E)} \int_{R_a}^{R_0} \frac{\Gamma(R) dR}{\hbar v(R, b, E)} \right)$$

where  $v(R, b, E)$  is the local velocity given by

$$v(R, b, E) = v_0 \sqrt{1 - \frac{V^*(R)}{E} - \frac{b^2}{R^2}}$$

and  $v_0$  is the asymptotic velocity of the neutral collision partners. The  $f_{\text{HCl}^+(A)}$  parameter represents the probability that the ionization produces the excited [Ne...HCl<sup>+</sup>(A)] complex. This factor has been experimentally found to be 0.39 for thermal energy collisions.<sup>6</sup> The cross section is then given by

$$\sigma_{\text{NeH}^+}(E) = 2\pi \int_0^{\infty} P_{\text{NeH}^+}(b, E) b db$$

**Model B:** The probability  $P_{\text{NeH}^+}(b, E)$  is multiplied by the probability that the complex, once formed through close collisions, dissociates to NeH<sup>+</sup>. For this reason our previous model has been improved by introducing this probability,  $P_{\text{PST}}(b, E)$ , as calculated following the schemes of the phase space theory (PST). This probability has been calculated for each impact parameter as

$$P_{\text{PST}}(b, E) = \frac{N_{\text{NeH}^+}}{N_{\text{HCl}^+} + N_{\text{NeH}^+}}$$

where  $N_{\text{NeH}^+}$  and  $N_{\text{HCl}^+}$  are the numbers of energetic states accessible by energy and angular momentum conservation from the ionic complex of specified energy and total angular momentum. For each impact parameter corresponding to the formation of the ionic complex with probability  $P_{\text{NeH}^+}$ , assuming that the ionization occurs at  $R_0(b)$ , the complex has a total energy

$$E_{\text{tot}} = E - E^*(R_0) - V_+(R_0) + E_{\text{vib}} + E_{\text{rot}}$$

where  $E_{\text{vib}}$  is the vibrational energy of HCl<sup>+</sup>(A) and  $E_{\text{rot}}$  its rotational energy. The total angular momentum is composed of the orbital angular momentum,  $L = \mu vb$ , and the rotational angular momentum of HCl<sup>+</sup>. In Table IV are reported the energies and vibrational populations of HCl<sup>+</sup>(A) and DCl<sup>+</sup>(A) as used for the calculation of the number of accessible states and the corresponding  $P_{\text{PST}}(b, E)$ . The populations of HCl<sup>+</sup>(A) are obtained from the data of ref 6 assuming that in our experiment a statistical population of the fine structure states of Ne\* is present. The

**TABLE IV: Vibrational Energy Level and Populations of HCl<sup>+</sup> and DCl<sup>+</sup> Used for the Model Calculation**

$v$	HCl <sup>+</sup>		DCl <sup>+</sup>	
	$E_{\text{vib}}, \text{eV}$	$f_v$	$E_{\text{vib}}, \text{eV}$	$f_v$
0	0.098	0.350	0.070	0.235
1	0.287	0.588	0.206	0.372
2	0.497	0.062	0.344	0.350
3			0.455	0.043

populations of DCl<sup>+</sup>(A) are obtained assuming that the ionization occurs following the Franck-Condon factors and using those reported in ref 6. The rotational energy of HCl<sup>+</sup>(A) and DCl<sup>+</sup>(A) has been assumed to be its thermal energy  $kT$ . For the calculation, the spectroscopic parameters reported in Table V have been also used.

In Figure 3 the branching ratio  $\sigma_{\text{NeH}^+}/\sigma_{\text{tot}}$  as experimentally obtained is compared with the calculation performed using the two models A and B. Both models give rise to results that are in satisfactory agreement with the experiment, when the experimental error is considered. The PST calculation (model B) leads to a decrease of the branching ratio obtained through the model A that is independent of the collision energy.

We note that the calculation of model B give results practically indistinguishable in Figure 4 for NeH<sup>+</sup> and NeD<sup>+</sup>. The observed absence of a measurable isotope effect is consistent with the phase space calculation.

## Discussion

The validity of the two-step mechanism lies primarily on the validity of the assumption of a local complex potential to describe the initial ionization event. This assumption is well justified by the "vertical" character of the ionization that leads to a Franck-Condon vibrational energy distribution for both excited- and ground-state hydrogen chloride ions. This enables the second part of the collision, step 2, to be initiated from well defined states of HCl<sup>+</sup>.

The major limitation of the present analysis is the use of spherical potentials. In fact, for the collision partner interaction in the entrance channel, both metastable spin-orbit and HCl orientation anisotropies are expected to be present. While the anisotropy arising from the internal spin-orbit structure of the neon metastable atoms should not play a determining role in thermal energy collisions, there may be more important dynamical effects associated with the two different possible orientations of HCl with respect to the incoming metastable atom. The assumption of a negligible spin-orbit anisotropy at thermal energies appears justified when one considers that a Ne\*(<sup>3</sup>P<sub>2,0</sub>) metastable atom has the excited electron in a 3s spherical orbital with a hole in the internal p orbitals: the anisotropy is due to the internal hole only, and therefore is expected to be rather small for thermal energy collisions where large internuclear distances are mainly probed.<sup>24</sup> Anisotropy effects should become operative only at short range, where the 3s orbital shielding is weak and the internal hole in the p orbitals becomes more important. Neglecting the HCl orientation anisotropy appears to be less clearly justified. Recent experimental results on the collisional autoionization of diatomic molecules with He\*(<sup>3</sup>S, <sup>1</sup>S) have shown that "end-on" or "side-on" collisions can lead to different energy dependences of the ionization cross sections, according to the different electron density distribution of the orbitals involved in the ionization.<sup>25</sup> Although no experimental or theoretical information is available for the present system, we note that the ionization product branching is not expected to be critically influenced by these details. Indirect evidence that the use of a spherical interaction to describe the Ne\*(<sup>3</sup>P<sub>2,0</sub>)-HCl optical potential is substantially reasonable is the observed good agreement between the calculated and experimental branching ratio.

In model A the only requirement to produce NeH<sup>+</sup> is the formation of an excited ionic complex followed by a "close approach" of the two partners. The fraction of autoionizing

collisions leading to excited complexes is 0.39 as obtained from the electron spectroscopy data by Yench et al.<sup>6</sup> This fraction has been determined assuming a statistical population of neon metastable spin-orbit states and using the electron energy spectrum measured at the single average collision energy of 0.055 eV. Owing to the lack of other information it has been assumed that the electronic and vibrational state distributions of HCl<sup>+</sup> ions do not vary significantly over the presently investigated energy range.

The use of PST, in model B, is justified by participation of the Ne–HCl<sup>+</sup>(A) ionic intermediate as characterized by the results obtained in the preliminary study of its structure and energy. In fact the complex appears to be weakly bound with a barrier along the exit channel toward NeH<sup>+</sup> formation. Moreover the complex is formed with very low kinetic energy according to the consideration that the ionization mostly occurs at the turning point. This could allow the complex to survive long enough to ensure a statistical redistribution of its internal energy.

The PST calculation requires the knowledge of the vibrational and rotational energy distributions of HCl<sup>+</sup>(A) within the excited complex. The vibrational energy distribution obtained by Yench et al.<sup>6</sup> from electron spectroscopy data has been used. In that work, two sets of electron spectroscopy data are presented, corresponding to different values of the collision energy, 0.055 and 0.130 eV, respectively. The two vibrational energy distributions agree within the experimental uncertainties, supporting our assumptions of an insignificant modification of internal energy distributions of nascent HCl<sup>+</sup> over the collision energy range of these experiments. For the rotational energy distribution of HCl<sup>+</sup>(A) ions, no data are available. Therefore  $E_{\text{rot}}$  has been simply expressed as its thermal average  $kT$ . However during the calculation it has been found that the initial rotational state of HCl<sup>+</sup>(A) does not play a significant role on the branching ratio among the two possible final products.

PST correctly predicts a negligible isotope effect. This can be attributed to the large number of states accessible to NeH<sup>+</sup> and HCl<sup>+</sup>(A). The isotopic substitution does not affect their ratio significantly.

In the PST analysis we found that the final product branching depends strongly on the vibrational levels of HCl<sup>+</sup>(A). For both the isotopic variants, the ground-state vibrational levels of HCl<sup>+</sup>(A) and DCl<sup>+</sup>(A) lead almost completely to H<sup>+</sup> or D<sup>+</sup> transfer rather than simple dissociation of the complex to Ne + HCl<sup>+</sup>(A) or DCl<sup>+</sup>(A). The probability of NeH<sup>+</sup> formation compared to HCl<sup>+</sup>(A) then decreases with increasing vibrational level. This result is not surprising when it is considered that the channel leading to NeH<sup>+</sup> is exothermic, while that of HCl<sup>+</sup> is endothermic (see Figure 4). The higher the energy of the complex, the higher the probability to dissociate to HCl<sup>+</sup>(A). From this consideration, one should expect a decreasing trend of the branching ratio with increasing collision energy as experimentally observed. However, we note that models A and B branching ratios show the same energy dependence, indicating that this dependence is more influenced by the change of the critical impact parameter for close collision than statistical factors. The substantial agreement of both the model calculations with the value and energy dependence of the measured branching ratio is a clear indication that the formation of NeH<sup>+</sup> is mainly governed by a "capture" mechanism after the electron ejection.

## Conclusion

The dynamics of NeH<sup>+</sup> production have been studied here by two models that couple simple theoretical ion–molecule reaction schemes with the semiclassical treatment of Penning and associative ionization. In model A, the so-called Langevin criterion, frequently used in the ion–molecule reaction analysis, has been taken into account; in model B, the theoretical approach of PST has also been used. The application of the statistical PST is justified by the results of a preliminary quantum study of the [Ne–HCl<sup>+</sup>(A)] ionic intermediate that appears to be a linear weakly bound complex. Both the models presented here agree

**TABLE V: Molecular Parameters Used for the Model Calculation**

	$\omega_e$ , cm <sup>-1</sup>	$\omega_e x_e$ , cm <sup>-1</sup>	$B$ , cm <sup>-1</sup>	ref
HCl <sup>+</sup> (A)	1605	40.3	7.50	21
DCl <sup>+</sup> (A)	1151	28.9	3.85	21
NeH <sup>+</sup>	2896	122	18.52	22, 23
NeD <sup>+</sup>	2096	88.3	9.70	22, 23

with the measured NeH<sup>+</sup> branching ratio value and its collision energy dependence within the experimental errors. The substantial agreement of the two models with the experimental data does not allow discrimination between them. However their identical energy dependence indicates that the NeH<sup>+</sup> formation is governed more by the "capture" mechanism than by statistical factors.

The present study has been performed through the measurement of Ne\*(<sup>3</sup>P<sub>2,0</sub>)–HCl integral elastic cross sections and NeH<sup>+</sup> product branching ratios as a function of collision energy. These data have been analyzed also taking into account the previously measured total and partial ionization cross sections<sup>4</sup> and the electron spectroscopy results by Hotop and co-workers.<sup>6</sup> These different experimental data are capable of giving information on individual events in the sequence of processes leading to reaction products. This work demonstrates how this procedure can lead to a rather complete characterization of the microscopic mechanism for the formation of the final product ions.

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## References and Notes

- (1) Aquilanti, V.; Brunetti, B.; Vecchiocattivi, F.; Letardi, T.; Fang, H.; Fu, S. *Chem. Phys. Lett.* **1993**, *205*, 229.
- (2) Brunetti, B.; Vecchiocattivi, F. In *Cluster Ions. Current Topics in Ion Chemistry and Physics*; Ng, C. Y. Ed.; Wiley: New York, 1993; Vol. 1, pp 359–445.
- (3) Siska, P. E. *Rev. Mod. Phys.* in press. Siska, P. E. *Comm. At. Mol. Phys.* **1984**, *15*, 155.
- (4) Aguilar, A.; Brunetti, B.; Falcinelli, S.; Gonzalez, M.; Vecchiocattivi, F. *J. Chem. Phys.* **1992**, *96*, 433.
- (5) Martin, D. W.; Weiser, C.; Sperlein, R. F.; Bernfeld, D.; Siska, P. E. *J. Chem. Phys.* **1989**, *90*, 1564. Martin, D. W.; Bernfeld, D.; Siska, P. E. *Chem. Phys. Lett.* **1984**, *110*, 298.
- (6) Yench, A. J.; Ganz, J.; Ruf, M. W.; Hotop, H. *Z. Phys. D* **1989**, *14*, 57.
- (7) Snyder, H. L.; Smith, B. T.; Martin, R. M. *Chem. Phys. Lett.* **1983**, *94*, 90.
- (8) Simon, W.; Yench, A. J.; Ruf, M. W.; Hotop, H. *Z. Phys. D* **1988**, *8*, 71.
- (9) Aguilar-Navarro, A.; Brunetti, B.; Rosi, S.; Vecchiocattivi, F.; Volpi, G. G. *J. Chem. Phys.* **1985**, *82*, 773.
- (10) Appolloni, L.; Brunetti, B.; Hermanussen, J.; Vecchiocattivi, F.; Volpi, G. G. *J. Chem. Phys.* **1987**, *87*, 3804.
- (11) van den Biesen, J. J. H. In *Atomic and Molecular Beam Methods*. Scoles, G., Ed.; Oxford University Press: London, 1988; Vol. 1, p 472.
- (12) Baudon, J.; Feron, P.; Miniatura, C.; Perales, F.; Reinhardt, J.; Robert, J.; Haberland, H.; Brunetti, B.; Vecchiocattivi, F. *J. Chem. Phys.* **1991**, *95*, 1801.
- (13) Cambi, R.; Cappelletti, D.; Liuti, G.; Pirani, F. *J. Chem. Phys.* **1991**, *95*, 1852.
- (14) Aquilanti, V.; Beneventi, L.; Grossi, G.; Vecchiocattivi, F. *J. Chem. Phys.* **1988**, *89*, 751.
- (15) Brunetti, B.; Falcinelli, S.; Paul, S.; Vecchiocattivi, F.; Volpi, G. G. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1505.
- (16) Eland, J. H. D.; Frey, R.; Kuestler, A.; Schulte, H.; Brehm, B. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 155.
- (17) Lane, I. C.; Powis, I. *J. Phys. Chem.* **1993**, *97*, 5803.
- (18) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.
- (19) Dunning, T. H., Jr. *Chem. Phys. Lett.* **1970**, *7*, 423.
- (20) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.
- (21) Shearley, W. D.; Matheus, C. W. *J. Mol. Spectrosc.* **1973**, *47*, 420.
- (22) Peyerimhoff, S. *J. Chem. Phys.* **1965**, *43*, 998.
- (23) Rosmus, P.; Reinsch, E. A.; Werner, H. J. In *Molecular Ions*. Berkowitz, J.; Groeneveld, K. O., Eds.; Plenum Press: New York, 1993; p 407.
- (24) Gregor, R. W.; Siska, P. E. *J. Chem. Phys.* **1981**, *74*, 1078. Kerstel, E. R. Th.; Janssens, M. F. M.; van Leeuwen, K. A. H.; Beijerinck, H. C. W. *Chem. Phys.* **1988**, *119*, 325.
- (25) Dunlavy, D. C.; Martin, D. W.; Siska, P. E. *J. Chem. Phys.* **1990**, *93*, 5347. Ohno, K.; Takami, T.; Mitsuke, K.; Ishida, T. *J. Chem. Phys.* **1991**, *94*, 2675.