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LOW ENERGY ION-MOLECULE REACTION DYNAMICS
AND
CHEMIIONIZATION KINETICS

Progress Report

James M. Farrar
University of Rochester
Rochester, New York

MASTER

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Abstract

We have completed the characterization of our crossed molecular beam apparatus and have begun low energy studies of proton transfer and charge exchange reactions of H_2^+ . We have completed a study of $H_2^+(CO,H)HCO^+$ in the relative energy range from 0.7 to 9.2 eV. The results of this study have been submitted for publication.^{1,2} Work has been initiated on the systems $H_2^+ + He, Ne, Ar, N_2,$ and O_2 and the first three of these systems will be completed by the end of this contract period.

We have also begun construction on a tandem-mass spectrometer for the study of associative detachment reactions. We intend to begin this project with a study of the reaction

using two-photon ionization laser induced mass spectrometric detection of reaction products. This technique will allow us to measure the distribution of (v',J') states in the product Na_2 species.

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Introduction

During the second year of our contract with the Department of Energy which began on February 1, 1979, we have focused attention on molecular collision studies of low energy ion-neutral interactions. We have placed special emphasis on low energy proton transfer and charge exchange reactions of H_2^+ with atoms and diatomic molecules. We have achieved successful operation of our low energy ion-neutral crossed beam apparatus below 1 eV in beam production and product detection.

Aside from teaching responsibilities associated with the Principal Investigator's appointment in the Department of Chemistry at the University of Rochester, the research supported by DOE in the contract occupies the full effort of the Principal Investigator. The same commitment of time will hold for the remainder of the contract year terminating on January 31, 1980.

Our work on proton transfer reactions has been quite successful. The operating parameters of our apparatus are quite well established and we have completed a detailed study of the H_2^+ (CO,H)HCO⁺ and H_2^+ (CO,H₂)CO⁺ systems in the energy range from 0.74 to 9.25 eV. This work has resulted in two papers which have been submitted for publication.^{1,2} This work has revealed a substantial amount of information about the dynamics of proton transfer reactions over an extended energy range. We have observed that the proton transfer reaction is direct at all energies, with dynamics in qualitative agreement with the

"Elastic Spectator Model".³ We have demonstrated that at rather low collision energies, the HCO^+ product is formed by rather impulsive collisions in which CO removes a proton from H_2^+ , leaving the H-atom spectator with the center of mass speed which H_2^+ had before the collision.

This stripping mechanism leads to very highly internally excited HCO^+ products at low energies, in which about 10% of the available energy in the collision appears as product translation. At a certain energy governed solely by momentum conservation and reactant internal excitation, the HCO^+ product internal excitation exceeds the bond dissociation energy (with respect to $\text{H}^+ + \text{CO}$) and products are no longer stable. The $\text{H}_2^+ (\text{CO}, \text{H})\text{HCO}^+$ system is exoergic by 3.6 eV and its dynamics appear to be of a nature which places a substantial amount of the exoergicity into forward recoil beyond the stripping limit. Thus, the "trans-stripping" behavior of the reaction can be described as product stabilization by forward recoil. The cross section for these highly translationally excited products is substantially smaller than the cross section for spectator stripping. We also find that in the "trans-stripping" regime, ~50% of the available energy appears as relative product translational energy.

The nature of the electronic surfaces leading to chemical reaction has been examined via electronic state correlations.

We have exploited the photoionization studies of formaldehyde performed by Guyon, Chupka, and Berkowitz⁴ and analyzed in some detail by the computations of Vaz Pires *et al.*⁵ The details of this discussion may be found in Ref. 2, but briefly, the C_{2v} surfaces of H_2CO^+ , when reduced to a lower symmetry by asymmetric collision geometries, provide a low energy pathway for the production of HCO^+ products in their ground electronic state.

We have also measured differential cross sections for the systems $H_2^+(Ar,H)HAr^+$ and $H_2^+(Ar,H_2)Ar^+$ over the energy range 0.7 to 6 eV. These experiments have been performed with an H_2^+ beam generated by electron impact on H_2 . This technique yields H_2^+ in a distribution of vibrational states, the most probable of which is $v=2$. The photoionization work of Chupka⁶ demonstrates that the rate of formation of HAr^+ shows no appreciable dependence on the H_2^+ vibrational state, in contrast with proton transfer to He or Ne, where the reaction is enhanced substantially by vibrationally excited reagents. While the rate of formation of HAr^+ does not depend on the state of H_2^+ , recent theoretical work by Baer⁷ suggests that the final vibrational state distribution of HAr^+ does depend strongly on the state of H_2^+ . This theoretical work indicates that H_2^+ in $v=0, 1$ yields vibrationally "cold" products while $H_2^+(v=2)$ results in a substantially "hotter" distribution. This prediction can be measured semi-quantitatively by measuring product ion translational energy distributions. We will use the technique of

Herman⁸ to produce partially state selected H_2^+ ions. This technique quenches H_2^+ for $v \geq 2$ via the reaction:

By using a 9:1 mixture of Ne: H_2 at high pressure, we expect to form beams of H_2^+ in $v=0$ and 1. These beams will allow us to test the predictions of Baer.

We have also begun complete differential cross section studies on the following reactions:

We expect that a thorough study of the first two of these reactions will be complete by the end of this contract year. The $H_2^+(He)$ system, although well studied, appears to possess some features apparently not observed in earlier studies. In particular, up to 10 eV (c.m.), the mechanism of the reaction seems to be in accord with spectator stripping, as noted by Herman et al.⁹ At about 10 eV, we have observed a second channel for HeH^+ production in which the products are scattered substantially backward of the HeH^+ product from spectator stripping. As the energy increases, this new mechanism dominates HeH^+ production as the spectator stripping peak decreases

in relative magnitude. We are currently seeking more data in an attempt to explain this interesting phenomenon.

Our proposal submitted last year included a description of some proposed experiments on the phenomenon of associative detachment, with special emphasis on the reactions of alkali anions with alkali atoms, e.g.,

Although our budget has not allowed us to purchase the laser we requested for the two-photon ionization studies of product state distributions, we have made progress in fabricating the apparatus for these studies. We have salvaged an Hitachi RMU-6E magnetic mass spectrometer which we are adapting for these experiments. We have modified the vacuum system and have designed an ion source for alkali anion production. We expect this work to be completed in the next few months.

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