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ELECTRON CAPTURE IN ION-MOLECULE COLLISIONS AT INTERMEDIATE ENERGY\*

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Abstract

Recent progress of theoretical charge transfer study in ion-molecule collisions at the intermediate energy is reviewed. Concept of close and distant collisions obtained from extensive ion-atom collision studies is identified so that it can be utilized to model two distinct collision processes. For a close collision, explicit representation of the whole collision complex is necessary to describe collision dynamics correctly, while a model potential approach for molecule is appropriate for a distant collision. It is shown that these two distinct models are indeed capable of reproducing experimental charge transfer cross sections. Some remarks for further theoretical study of ion-molecule collisions are also given.

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## I. INTRODUCTION

Owing to recent significant progress in both experimental and theoretical studies of ion-atom collisions at intermediate energies, our understanding of collision dynamics of various inelastic events in ion-atom collisions has been extensively broadened. In contrast to the flourishing ion-atom collision study,<sup>1</sup> comprehensive theoretical studies of ion-molecule collisions are extremely rare. Undoubtedly, difficulties arising from obtaining accurate electronic wavefunctions of colliding ion-molecule system and the complexity of practical computations are responsible.<sup>2,3</sup> However, concepts of close and distant collisions describing collision mechanisms in ion-atom collisions would be surely applicable for study of ion-molecule collisions.<sup>2-5</sup> For a close collision where the molecular nature of triatomic collision system plays an important role, explicit representation of the whole ion-molecule system is indispensable to the correct determination of the collision dynamics. State-of-the art technology developed in quantum chemistry can be adopted to generate reasonably accurate electronic wavefunctions as well as adiabatic potentials of the colliding system. For a distant collision where important collision dynamics takes place at large internuclear separation and correspondingly, the molecular nature of a colliding system does not greatly influence the collision dynamics, a simple model analogous to that for an ion-atom collision system may be used to describe the collision dynamics of ion-molecule collision reasonably well. The model is to approximate the molecule by a model potential and neglect the strong coupling region of ion-molecule collisional complex. Practically, the lower ( $Z = 1, 2$ ) charged ion-molecule collision system belongs to the former category, while the higher ( $Z \geq 3$ ) charged ion-molecule collision system to the latter. We have applied the diatoms-in-molecules (DIM) method,<sup>6-9</sup> as well as the more sophisticated ab

initio molecular structure method,<sup>10,11</sup> to obtain accurate molecular wavefunctions and potential surfaces as functions of internuclear distances and molecular orientations explicitly to investigate close collisions. A pseudo potential or model potential method<sup>12,13</sup> has been employed to represent the molecular-ion core, which allows us to treat a target molecule as an atom having an ionization potential of forming a molecular ion. This treatment is quite adequate for describing distant ion-molecule collisions.<sup>14,15</sup> In this review, we will give representative examples from each collision mechanism where a detailed comparison between experimental and theoretical results is possible. Through this comparison, it is hoped that the validity, as well as the difficulty, of each model is identified, and some guidelines are provided for future work.

## II. THEORETICAL TREATMENT

Molecular wavefunctions and corresponding eigenenergies (potential surfaces) have been obtained by using the diatoms-in-molecules (DIM) method<sup>8</sup> for a close collision problem. Based on the valence-bond idea, the DIM method has been widely used recently because of its simplicity and ability in generating reasonably accurate potential surfaces for polyatomic systems. In the DIM method, the electronic Hamiltonian is partitioned into atomic and diatomic terms. This partitioning of the electronic Hamiltonian is exact. Probably the most crucial approximation used in the DIM method is the fact that the partitioned atomic and diatomic fragments are fully determined by using properties of the isolated fragments. Also, zero overlap of the atomic orbitals is usually assumed. This method may not be accurate when the fragments interact strongly at small separation, i.e.  $R \leq R_e$  ( $R_e$ : equilibrium separation), but is expected to be valid at "large" separation where the

critical collision dynamics usually take place. Nevertheless, quite good agreement with large scale ab initio calculations has been obtained for molecular geometries and energies.<sup>2</sup> For a distant collision problem where the molecular effect of colliding particles is weak, the pseudo potential or model potential method<sup>12-15</sup> was used to represent the fixed-nucleus molecular-ion core which enables us to treat the molecule as an atom having an ionization potential of  $XY \rightarrow XY^+$  (where  $XY$  is a molecule). This approximation is felt to be valid since only distant collisions are expected to be important. The molecular electronic Hamiltonian containing the pseudo potential was diagonalized employing the standard linear-combination of atomic-orbital (LCAO) method to obtain molecular wavefunctions and adiabatic potentials of colliding systems.

For collisions between ions and molecules where the collision energy is above 0.1 keV/amu, it is adequate to treat the motion of the heavy particles classically. Because many states contribute to the determination of the collision dynamics, it is clear that the close coupling technique has to be employed to tackle ion-molecule collision problems. In the close coupling method, the scattering wavefunction is expanded in terms of the molecular adiabatic wavefunction as

$$\Psi(\vec{r}, \rho, t) = \sum_i a_i(t) \phi_i^{\text{Mol}}(\vec{r}, \rho, R) X_{V_i}(\rho) F_i(\vec{r}, R), \quad (1)$$

where  $F_i(\vec{r}, R)$  represents electron translation factors (ETF's) and  $X_{V_i}(\rho)$  denotes the vibrational wavefunction of a molecule.  $\vec{r}$  and  $\rho$  denote the coordinates of electron and vibrating molecule, respectively. The ETF describes the translation effect of the electron moving with a particular nucleus or molecule, and ensures that the scattering wavefunction satisfies

the correct scattering boundary conditions. The inclusion of the ETF in the expansion is not only a matter of formality, but also of practical importance. Without the ETF, the coupling matrix shows origin dependence of the chosen electron coordinates. Hence, the calculated probability cannot be determined uniquely.<sup>16</sup> Substituting the scattering wavefunction [Eq. (1)] into the time-dependent Schrödinger equation, one obtains linear first-order coupled equations similar to those seen in ion-atom scattering problems<sup>16</sup> except for the presence of overlap terms involving the vibrational wavefunctions of the target molecule. These coupled equations are solved numerically to yield the scattering amplitude and hence, probability.

### III. SELECTIVE EXAMPLES

In this section, we discuss representative examples of calculated results based on the molecular representation summarized previously, along with experiments to assess our understanding of the collision dynamics of ion-molecule collisions. Although the concept of close and distant collisions is somewhat vague, we tentatively define here a close collision when the dominant charge transfer occurs in the region of  $R \lesssim 5$  a.u. Otherwise they are defined as distant collisions.

The coordinates of the colliding system are shown in Figure 1.

#### A. Close Collisions

The adiabatic potential curves for the  $H_3^+$  system are shown in Figure 2 for several values of molecular angles  $\theta$  with  $\phi = 0$ . Note that molecular orientation effect is not noticeable until the heavy particles approach around  $R \sim 2$  a.u. A constant energy gap between the initial and charge transfer channels for values of  $R \gtrsim 3.5$  a.u. may induce the Demkov coupling effect,

which suggests the existence of a dominant peak in the radial coupling around  $R \sim 4$  a.u. region.<sup>2</sup> Indeed, the calculated radial coupling matrix elements display a sharp peak at  $R \sim 3.5$  a.u., although their shapes and magnitudes largely depend on the molecular orientation for  $R < 4$  a.u.<sup>2</sup> The impact parameter times the transition probability is plotted at  $E = 1$  keV for several choices of  $\theta$  in Fig. 3. Generally, there are three main peaks corresponding to impact parameters of  $\sim 2$ ,  $\sim 3$ , and  $4.5$  a.u. for all orientations. These oscillatory structures seen in the probability is regarded as characteristics of the Demkov coupling effect. These two figures provide clear evidence for the fact that a close collision mechanism is indeed the dominant mechanism of charge transfer in the  $H^+ + H_2$  collision case. To test the energy dependence of the molecular effect, the probability times the impact parameter versus the impact parameter is shown in Fig. 4 for  $E = 10$  keV with different  $\theta$ . Two main peaks are found at  $b \sim 1$  a.u. and  $3.5-4.0$  a.u. for all  $\theta$ . The inner peak located at  $b \sim 1$  a.u. grows dramatically as the energy increases compared to the peaks in Fig. 3.

Usually, except for the energy matching region where the velocity of orbital electron and the relative velocity of heavy particles becomes close and charge transfer cross section shows its maximum, a close encounter of colliding partners is necessary for charge transfer to proceed effectively. This suggests that the close collision mechanism becomes more important for charge transfer process at energies below 1 keV and above 10 keV.

Total cross section summing all the vibrational states of the  $H_2^+$  ( $v' = 0 - 10$ ) molecular ion is plotted in Fig. 5 along with experimental measurements.<sup>17-20</sup> Our results are qualitatively in good accord with all measurements in the energy range where they are available. This apparently shows that our model to describe a close collision is physically sound.

However, in the energy regions where the present calculation does not cover this model may not offer accurate result due to neglect of other channels, namely, vibrational excitation or electronically excited states of atom or molecular ion, which are considered to be dominant processes in lower and higher energy regimes.

### B. Distant Collisions

It is well known from previous theoretical investigations of fully stripped ion-atom collisions that charge transfer takes place predominantly by means of avoided crossings located within a narrow range of internuclear separations at large internuclear distances ( $R > 5$  a.u.).<sup>1</sup> This feature of the collision dynamics evidently can be expected to hold for the  $H_2$  target as well, since the ionization potentials of H and  $H_2$  are similar. The adiabatic potential curves calculated by this model are shown in Fig. 6 for  $N^{7+} + H_2$  collision system.<sup>14,15</sup> The very narrow avoided crossing between initial and charge transfer channels can be observed at  $R \sim 15$  a.u. Actually, the avoided crossing at this point is so narrow that the nature of this avoided crossing is nearly diabatic in the present collision energy range. The important radial coupling between the initial and charge transfer channels has a sharp peak around  $R \sim 15$  a.u.<sup>15</sup> This distance is quite large compared to the size of the  $H_2$  molecule and therefore, the collision is expected to be over before the projectile encounters a "real" molecule. Corresponding total charge transfer probability at  $E = 5$  keV/amu is plotted in Fig. 7. The probability apparently dies off at  $R \sim 15$  a.u., reflecting the size of the important radial coupling. Contribution to the transition probability from the region where the molecular effect must be influential, i.e., region near  $R < 2$  a.u., may be  $\sim 10\%$  of the total transition probability.

In Fig. 8, we show the result of the total charge transfer cross section for the  $N^{7+} + H_2$  system. Agreement of the present result with recent measurement<sup>21</sup> is very good in both magnitude and shape. Application of this model to other systems displays consistently a good agreement with measurements for total charge transfer cross section.<sup>15</sup> This is encouraging for pursuing further detailed studies of ion-molecule collisions.

#### IV. SUMMARY

Two theoretical models applicable to study both close and distant collisions, respectively, have been proposed. For a close collision where explicit representation of a whole colliding system is necessary, the DIM method is suitable for its simplicity to obtain reasonably accurate molecular wavefunctions and adiabatic potentials. Although the DIM method has been successful for study of total charge transfer cross section, more rigorous ab initio treatment for describing the colliding system is certainly desirable. This is particularly so for a more specific and detailed study of the collision dynamics including differential cross section, and alignment and orientation of charge cloud. More sophisticated molecular codes developed in the quantum chemistry are suited for this specific purpose of collision problem.<sup>10,11</sup> Some works along this line are underway to study various inelastic events in  $He^+ + H_2$  and  $C^+ + H_2$  collisions, as a function of various collision parameters. Further exploration of detailed theoretical work is definitely necessary to deepen our understanding of the collision dynamics, as well as to give a rationale to varieties of yet unexplained experimental findings.

A model potential approach for the molecule seems to give reasonably good success for reproducing total charge transfer cross section in a distant

collision case. This clearly proves correct physics in a model potential approach to some extent. However, in order to provide a firmer base to the model, again, this model has to be explored with more stringent and extensive testing. Although there is no reason to believe that this model would give erroneous results for the determination of total charge transfer cross section for some distant collision cases, it may become necessary to relax constraints imposed on the model when some elements of a close collision come into the collision dynamics.

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## FIGURE CAPTIONS

- Figure 1. Coordinate in the laboratory frame for ion-molecule system.
- Figure 2. Adiabatic potential curves of the  $H^+ + H_2$  collision system as a function of internuclear distance  $R$  and angle  $\theta$  with fixed  $\phi = 0$ .
- Figure 3. Probability times impact parameter versus impact parameters as a function of  $\theta$  at  $E = 1$  keV and  $\phi = 0$ .
- Figure 4. The same as Fig. 3, except  $E = 10$  keV.
- Figure 5. Charge transfer cross section on the process  $H^+ + H_2 (X \ ^1\Sigma_g) + H(1s) + H_2^+(1\sigma_g)$  as a function of incident energy. Theory: solid line. Experiment:  $\times$ , Ref. 17;  $\blacksquare$ , Ref. 18;  $\circ$ , Ref 19;  $\nabla$ , Ref. 20.
- Figure 6. Adiabatic potentials for  $NH_2^{7+}$  as a function of internuclear distance.
- Figure 7. Charge transfer probability versus impact parameter for  $N^{7+} + H_2$  collision at  $E = 5$  keV.
- Figure 8. Total charge transfer cross sections in  $N^{7+} + H_2$  collisions. Theory: solid line. Experiment:  $\circ$ , Ref 21.

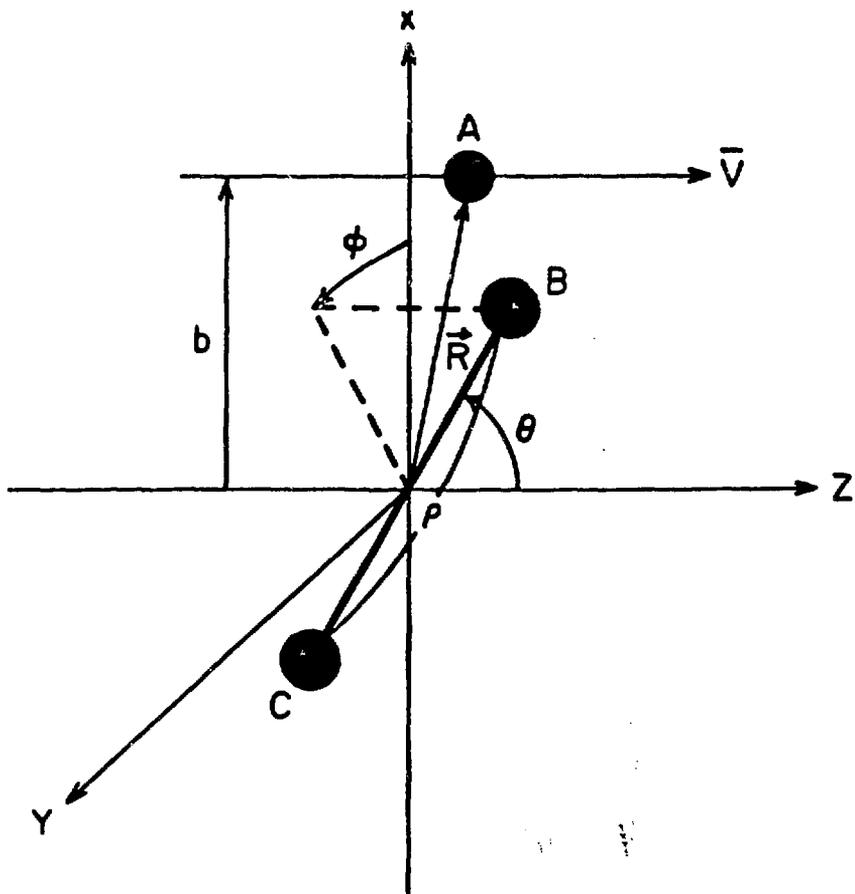


Fig. 1.

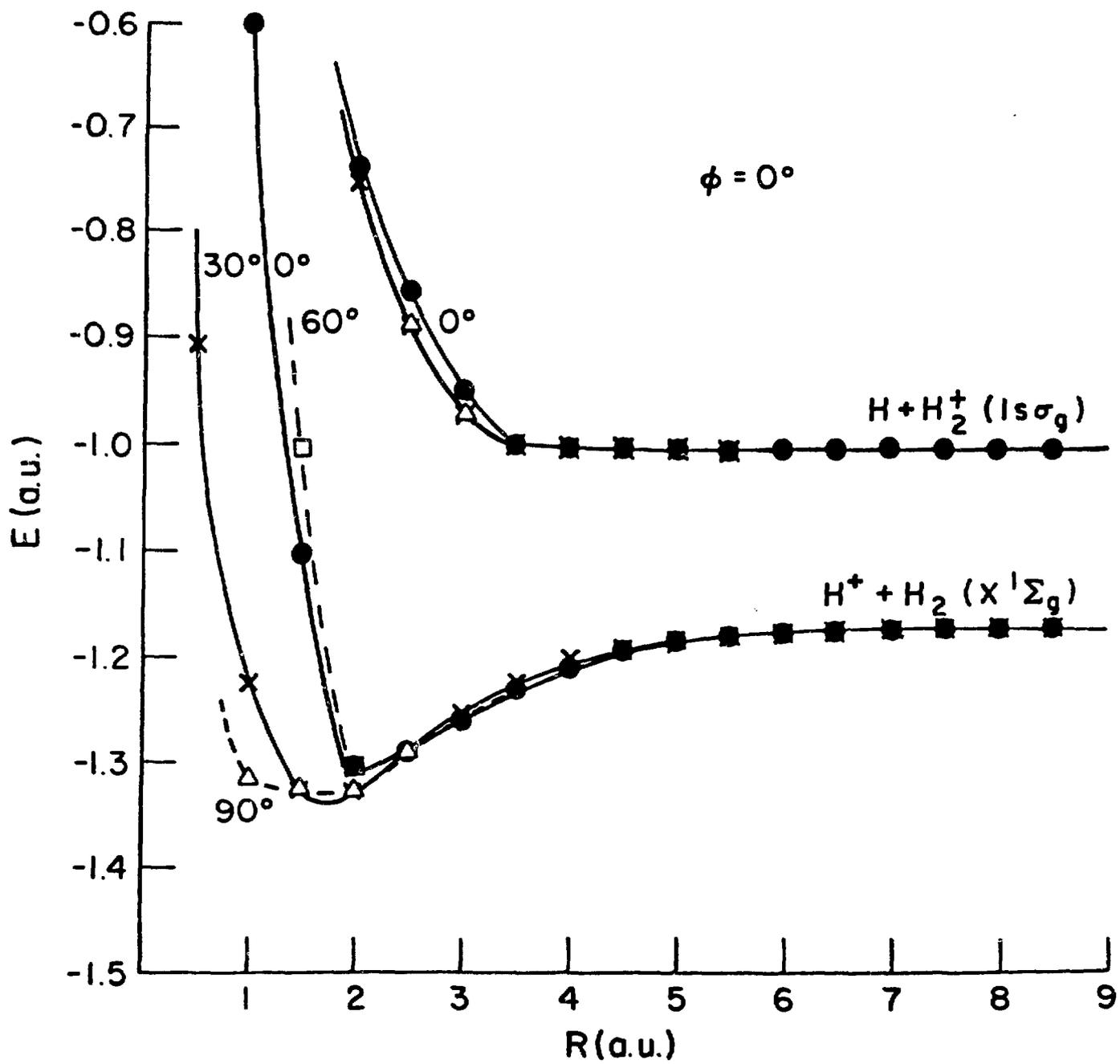


Fig. 2.

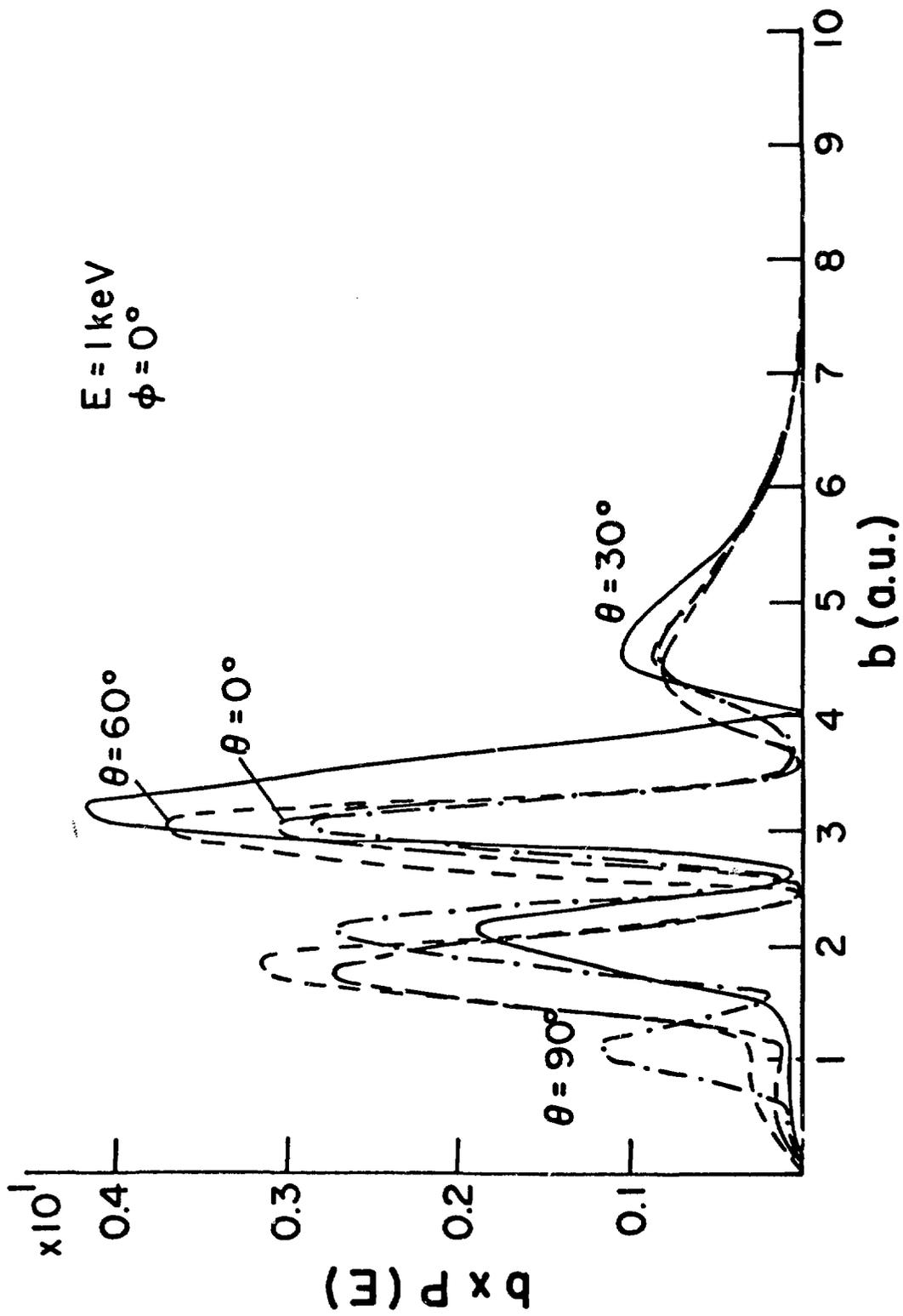


Fig. 3.

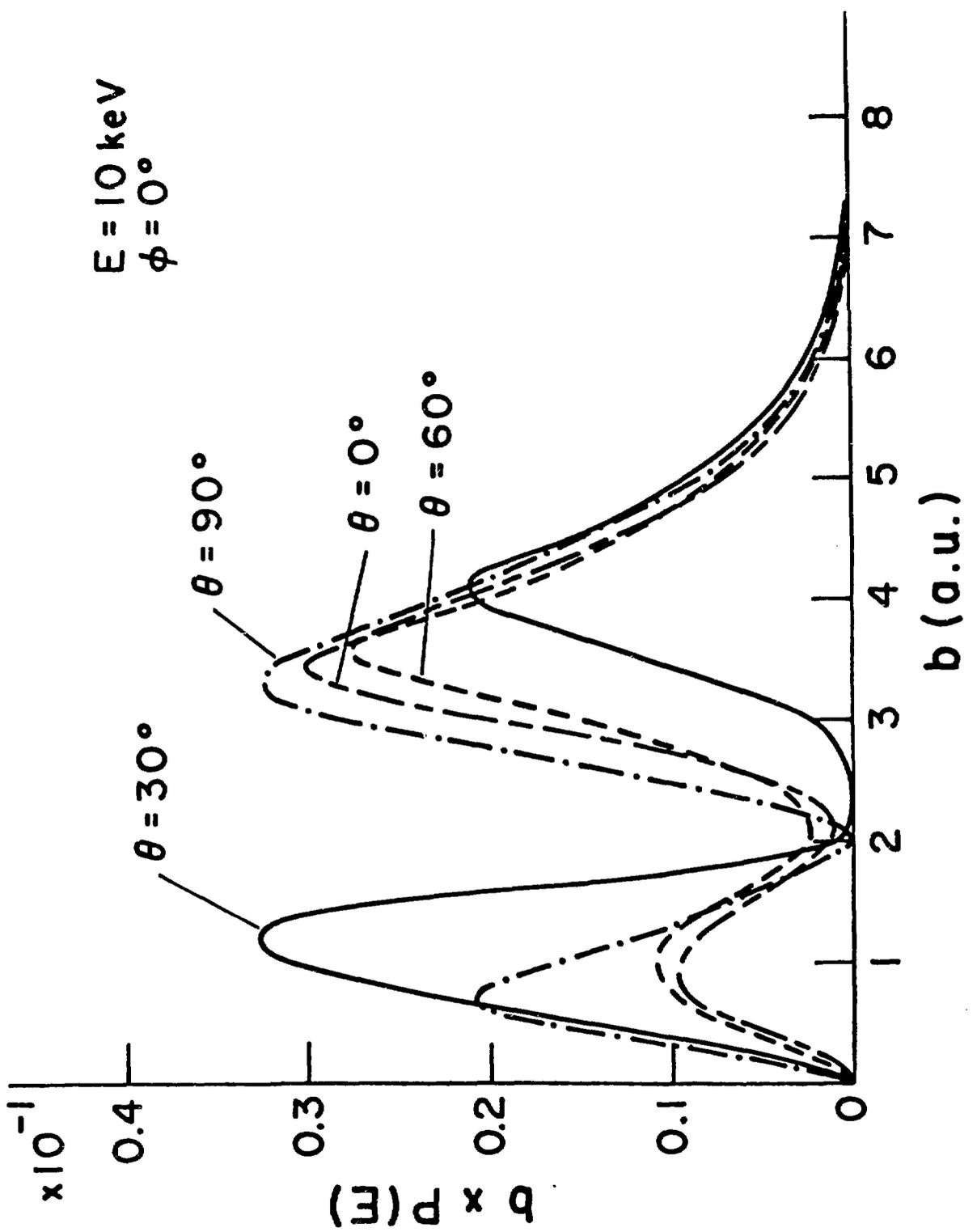


Fig. 4

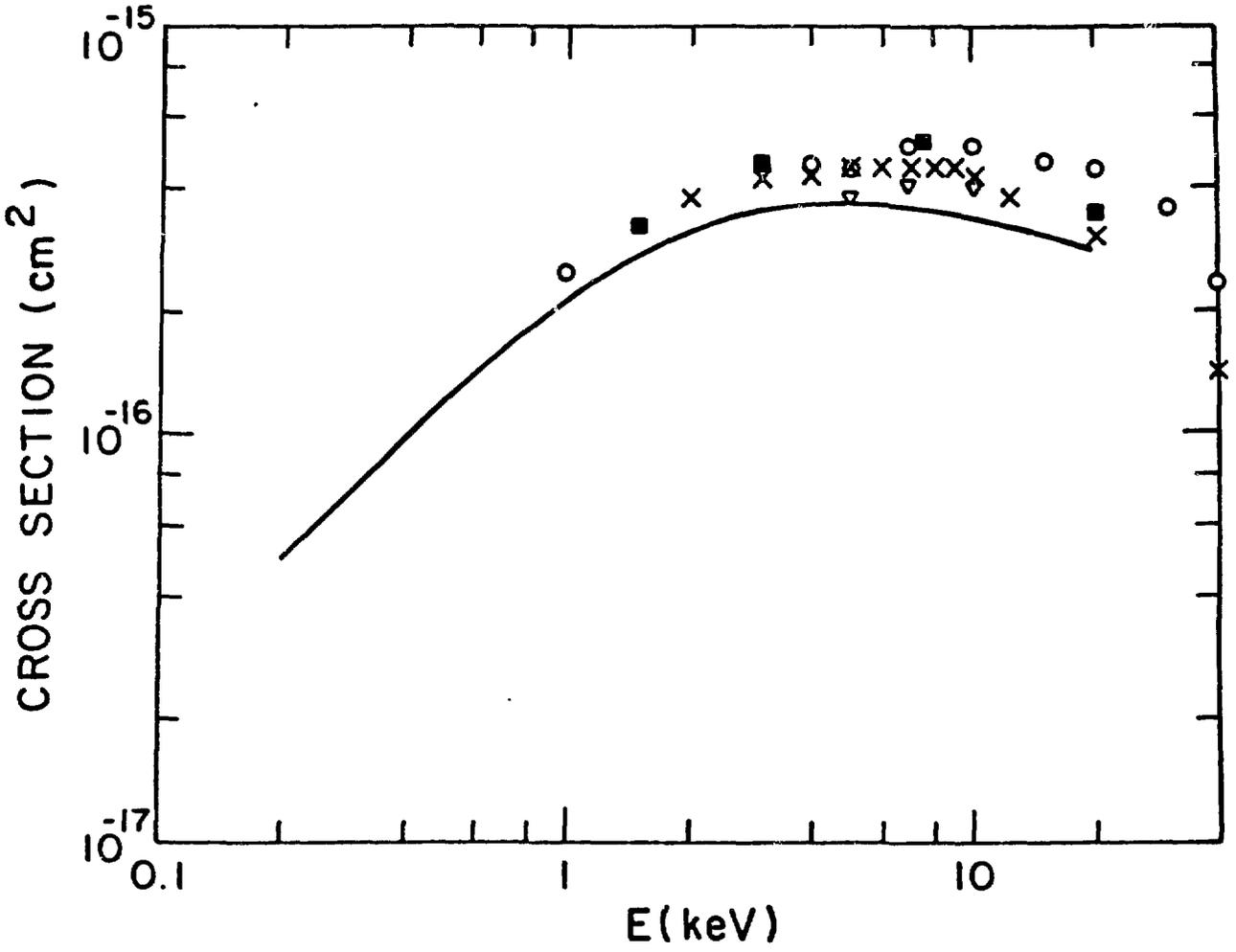


Fig. 5.

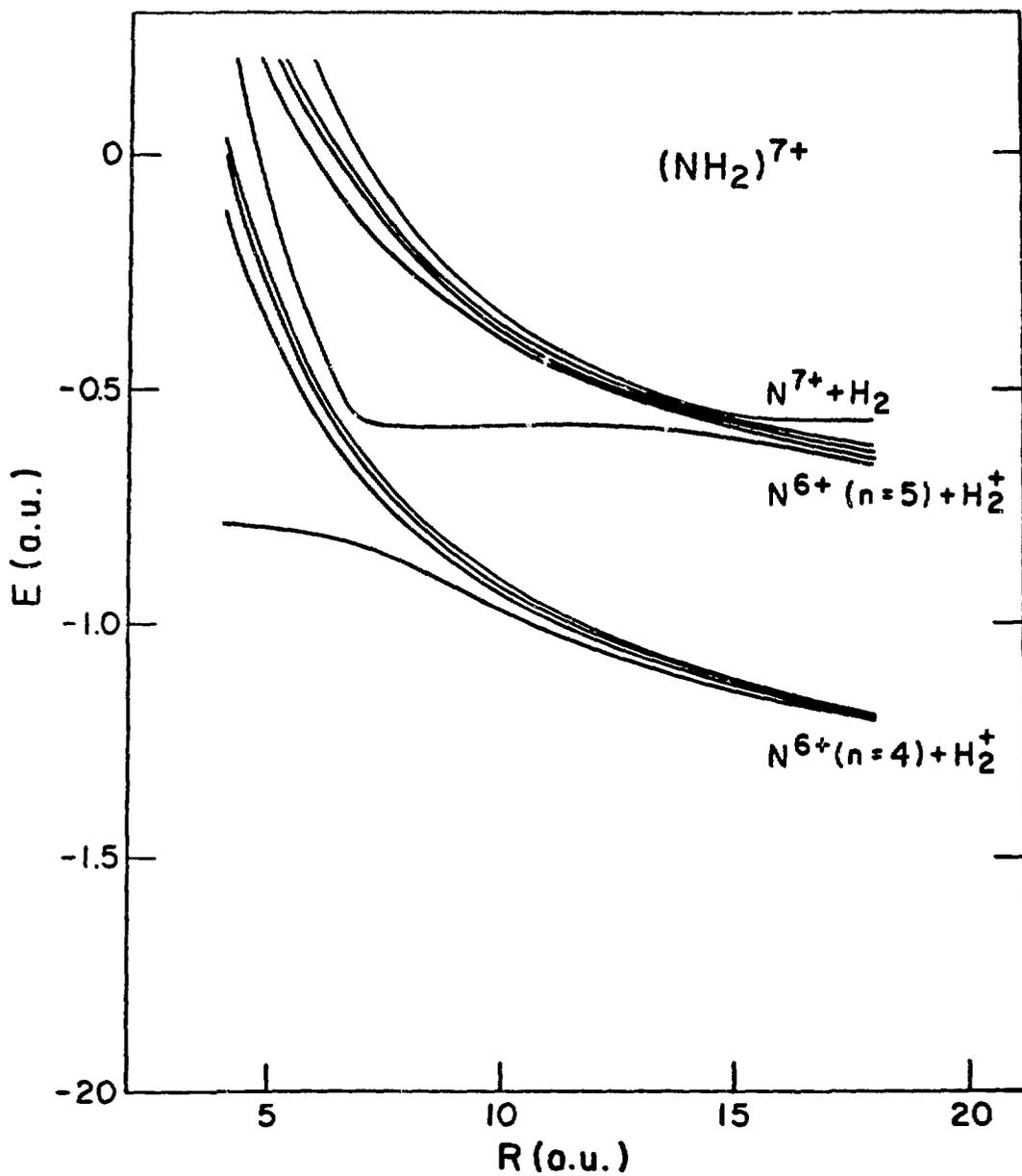
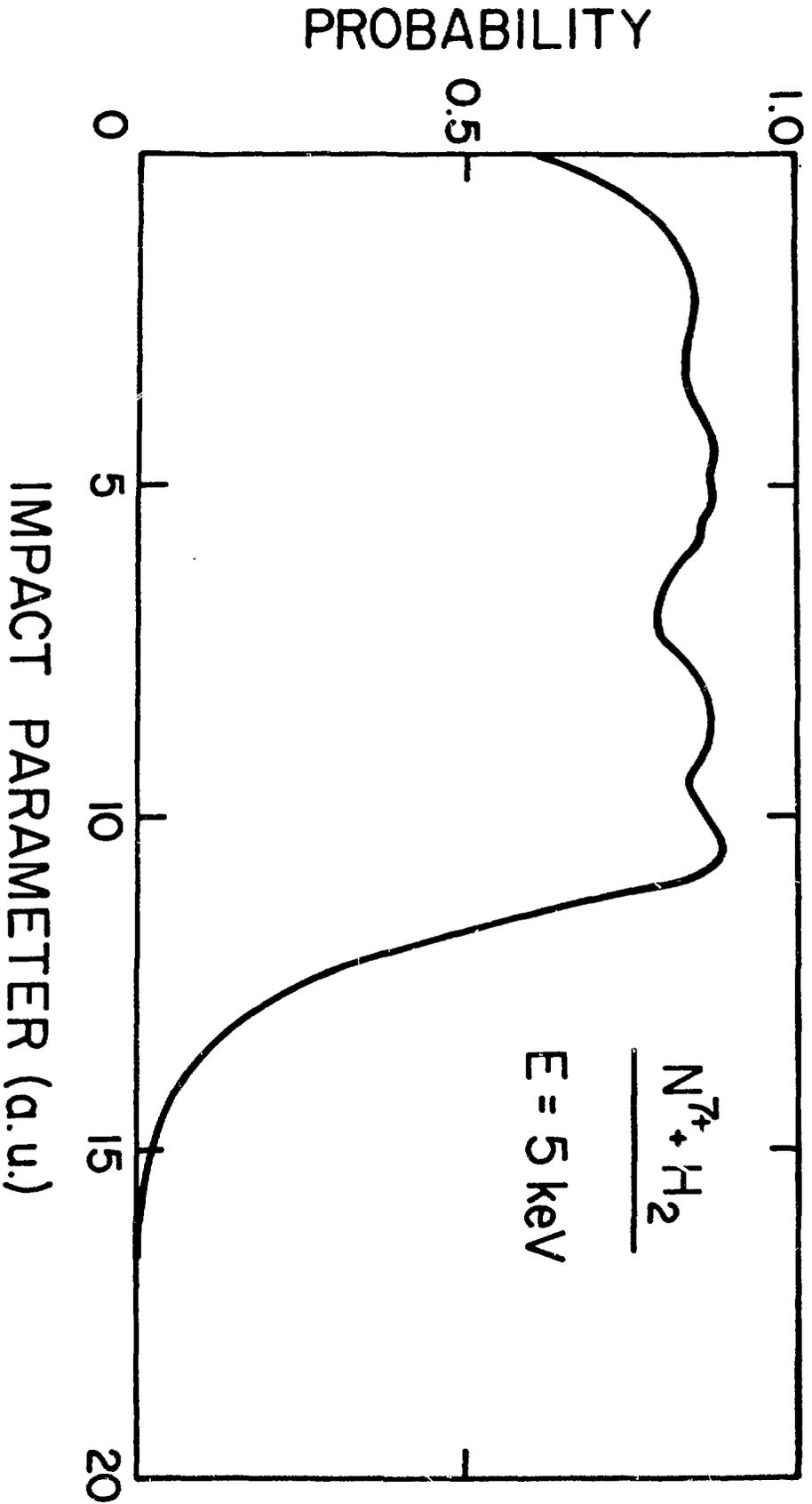


Fig. 6.



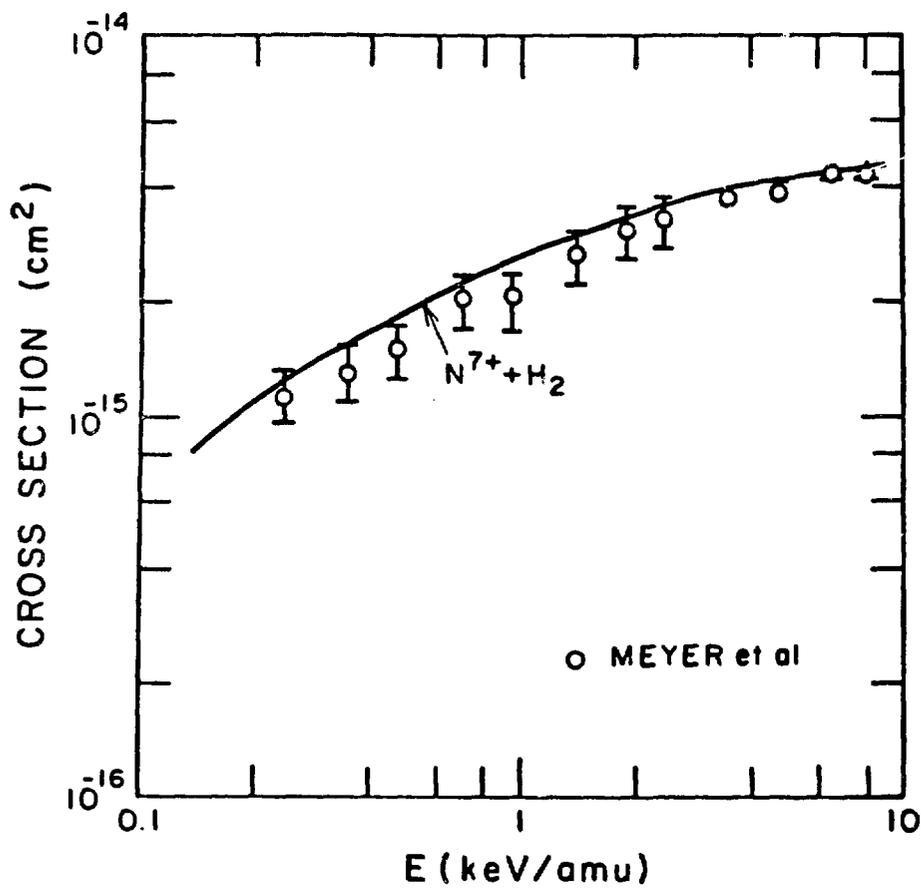


Fig. 8.