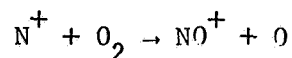


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A CROSSED BEAM STUDY OF THE REACTION



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ABSTRACT

The reaction  $\text{N}^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O}$  has been studied as a function of collision energy using the crossed beam apparatus EVA. This process is of considerable importance in the upper atmosphere. The system is also of particular interest because it may involve strong interactions between several intersecting or close-lying electronic surfaces of  $\text{NO}_2^+$ . This is not the case for previously well-studied ion-molecule reactions (e.g.,  $\text{Ar}^+ + \text{D}_2$ ), the dynamics of which are closely represented by simple models dominated by long-range electrostatic forces (e.g. "polarization-stripping").

Beams of  $\text{N}^+$  in the ground ( $^3\text{P}$ ) state were crossed with thermal  $\text{O}_2$  beams and the angular and velocity distributions of the  $\text{NO}^+$  product measured. The reaction exhibits the asymmetric distribution characteristic of a direct process. Its translational exoergicity ( $Q$ ) declines with energy, but above 5eV relative energy, becomes constant. These data were then corrected for angular and energy spreads of the beams. The position of the plateau in  $Q$  appears consistent only with production of  $\text{O}(^3\text{P})$  and a state of  $\text{NO}^+$  which, with excess energy, dissociates to  $\text{N}(^4\text{S}^0)$  and  $\text{O}^+(^4\text{S}^0)$ . Consideration of the correlation diagram for  $\text{NO}_2^+$  then indicates the following mechanism as probable: At moderately large separation  $\text{N}^+(^3\text{P})$  and  $\text{O}_2(^3\Sigma_g^-)$ , originally on a surface correlating with linear  $\text{NO}_2^+$  (excited  $^1\Sigma^+$ ), experience an electron jump leading to a surface correlating similarly with  $\text{NO}_2^+(^1\Sigma^-$  or  $^1\Pi)$ . Upon closer approach an O atom is transferred leading adiabatically to  $\text{O}(^3\text{P}) + \text{NO}^+(^3\Sigma^+)$ . (The latter will dissociate to  $\text{N}(^4\text{S}^0)$  and  $\text{O}^+(^4\text{S}^0)$  if sufficient energy is available.) Unlike the reaction to give ground state products, this process is only slightly exoergic. This accounts for the fact that so little of the potentially available energy appears as translation.

CASE FILE  
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Reactions of  $N^+$  with  $O_2$  are thought to be very important in the earth's upper atmosphere. At altitudes of about 300 km  $N^+$  is the second most abundant ion.<sup>1</sup> The favored mechanism for production of  $N^+$  ions at these altitudes is dissociative photoionization of  $N_2$ , which would result in  $N^+$  velocities much greater than thermal.<sup>1</sup> The primary  $N^+$  loss mechanism is reaction with  $O_2$ .<sup>1</sup>

Because of this atmospheric importance the reactions



and



have been the subject of extensive study.<sup>2-10</sup> The related reactions



and



have also been experimentally investigated.<sup>4,11</sup> As a result of this work, data exist on total cross-sections and their dependences on energy for these reactions. Very little is known, however, about their mechanisms.

In order to learn more about the dynamics of these reactions we have studied reaction (1) in a crossed-beam experiment. We find that this reaction proceeds by a direct, impulsive mechanism. There have been several simple models proposed to describe direct ion-molecule reactions, notably the "polarization stripping"<sup>12, 13</sup> and the "kinematic"<sup>14, 15</sup> models. These models have been quite successful in accounting for certain experimental results simply in terms of long-range forces and kinematics. Indeed, the very success of these models led to the fear that ion-molecule reactions might be a relatively insensitive probe of the nature of the shorter range interactions specific to a given system.

The study of reactions (1) - (4) may, however, be particularly helpful in understanding the "chemistry" of the  $NO_2^+$  system. None of these reactions can be classified as a "typical" ion-molecule reaction. Reactions (3) and (4) exhibit abnormally small cross-sections, indicating weak or repulsive effective potentials. Reactions (2) and (3) are charge transfer

reactions and therefore involve electronic transitions, something ignored by the simple models.

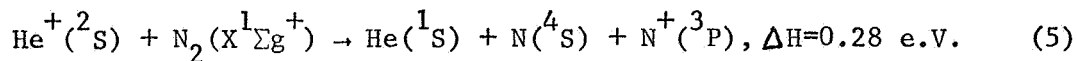
We conclude from the present study that reaction (1) also must involve a non-adiabatic electronic transition. We observe decomposition of  $\text{NO}^+$  product when its internal energy is just sufficient for it to dissociate to its ground state fragments. From knowledge of the  $\text{NO}^+$  electronic states, it can be seen that this requires that the  $\text{NO}^+$  product be formed in either of only two electronic states,  $X^1\Sigma^+$  or  $^3\Sigma^+$ , neither of which can be formed adiabatically from the initial channel. From consideration of the  $\text{NO}_2^+$  potential surfaces we further conclude that it is likely that reaction (1) involves an "electron jump" prior to "close collision," and that the resulting product is electronically excited  $\text{NO}^+(^3\Sigma^+)$ .

## I. EXPERIMENTAL

Experiments were performed with the crossed-beam apparatus EVA<sup>12</sup>. The experiments proceed basically as follows:  $\text{N}^+$  ions are formed by either of the two methods described below, mass analyzed in a  $180^\circ$  mass spectrometer and decelerated and focused into a beam of narrow angular and energy spread by a system of electrostatic lenses. In the collision region the ion beam is intersected at  $90^\circ$  by a modulated, thermal beam of oxygen (temperature about  $55^\circ\text{C}$ ). Ions from the collision zone pass through a detection slit, a stopping-potential energy analyzer and a  $60^\circ$  sector mass spectrometer before being detected by an electron multiplier. Phase sensitive detection of the  $\text{NO}^+$  product is employed to eliminate background problems, and a time averaging computer is used to improve the signal-to-noise ratio. Since the beam sources are mounted on the rotatable lid of the collision chamber, both angular and velocity distributions of the ionic products can be obtained. The apparatus is described in detail elsewhere.<sup>16</sup>

$\text{N}^+$  ions were produced by two methods. The first was from  $\text{N}_2^0$  by impact of 120 Volt electrons. Such a beam should contain 90%  $\text{N}^+(^3\text{P})$  and about 10%  $\text{N}^+(^1\text{S})$ , according to Lindholm's data.<sup>17</sup> The second was by 120 V. electron impact of a mixture of He and  $\text{N}_2$  ( $\text{P}(\text{He})/\text{P}(\text{N}_2) \sim 20$ ) at rela-

tively high pressures. This method makes use of the very fast reaction<sup>18</sup>



Since formation of the first excited  $^4\text{S}$  state of  $\text{N}^+$  by this reaction is 1.62 eV endothermic, we can be sure that all  $\text{N}^+$  ions so formed are in the ground state.

In using the latter technique, the ionization chamber of the primary ion source was modified by closing the ion exit slit to a circular aperture 0.5 mm in diameter, in order to decrease the gas leakage from the chamber. When the  $\text{He}/\text{N}_2$  gaseous mixture was ionized at lower pressures (about  $10^{-4}$  Torr in the ionization chamber), the energy spectrum of  $\text{N}^+$  produced was several eV broad. This corresponds to  $\text{N}^+$  (and perhaps some  $\text{N}_2^{++}$ ) formed directly by electron impact. However, when the pressure was increased a peak of lower energy and narrower spread appeared, due to  $\text{N}^+$  formed by the charge transfer between  $\text{He}^+$  and  $\text{N}_2$ . At optimum conditions (ionization chamber pressure about  $10^{-2}$  Torr) the broad  $\text{N}^+$  distribution was negligible in comparison with the  $\text{N}^+$  peak formed by charge exchange.

There was no observable difference in experimental results when  $\text{N}^+$  ions were produced by electron impact of  $\text{N}_2\text{O}$  rather than by reaction (4). Therefore, we conclude that most of the  $\text{N}^+$  ions produced by the former method are indeed formed in the ground state directly, or else relax to the ground state before entering the collision region. Roughly equivalent high intensity  $\text{N}^+(^3\text{P})$  beams with energies down to 1.8 eV could be obtained by either method.<sup>19</sup> Commercial grade bottled  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , He and  $\text{O}_2$  were used for these experiments.

## II. RESULTS

Energy and angular distributions of  $\text{NO}^+$  formed by reaction (1) were measured for initial relative energies between 1.2 and 8.3 eV. The data from two typical experiments are summarized in figures 1C and 2C by means of the usual velocity vector Newton diagrams.<sup>20</sup> Contour lines are constructed to represent the relative intensity of the  $\text{NO}^+$  product as a function of laboratory angle and velocity. These intensities are obtained as follows: the energy distribution measured at each fixed laboratory angle is converted to a velocity distribution by multiplying by the product laboratory velocity  $V$ . The resulting laboratory velocity distri-

bution is then converted to the cartesian system by dividing by  $V^2$ .<sup>21</sup> After normalizing so that the highest intensity = 100, contour lines of constant intensity are superimposed on a diagram showing the most probable laboratory  $N^+$  and  $O_2$  velocities, the most probable laboratory velocity of the center of mass  $V_{CM}$ , and the most probable  $N^+ - O_2$  relative velocity  $V_{rel}$ .

In addition to the "complete" experiments mentioned above in which both angular and energy distributions were measured, many "peak value" experiments were performed for which the product energy distribution was measured at only the one laboratory angle corresponding to maximum product intensity. The results of these experiments are shown in figure 3 in which the most probable translational exoergicity,  $Q_{mp}$ , is plotted against the most probable relative  $N^+ - O_2$  energy.  $Q$  is a purely experimental quantity defined by

$$Q = T_f - T_i$$

where  $T_i$  and  $T_f$  are the initial and final relative energies, respectively.

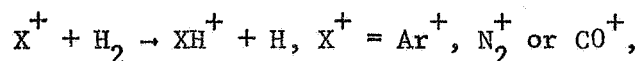
### III. INTERPRETATION

#### A. QUALITATIVE

Several important features of the mechanism of reaction (1) can be deduced immediately from the experiments. The  $NO^+$  product is observed to be virtually entirely "forward" of the center of mass velocity, indicating that the mechanism is direct: from the complete lack of symmetry with respect to the center of mass velocity, one can conclude that the vast majority of reactive collisions do not involve an  $NO_2^+$  complex with lifetime comparable to, or longer than, its rotation period ( $\sim 10^{-12}$  sec.).<sup>22</sup> This is true even at the lowest relative energy (1.2 eV) studied. Furthermore, for initial relative energies lower than about 5 eV,  $Q_{mp}$  as shown in figure 3 falls quite close to  $Q_{ss}$ , the value predicted by the simple spectator stripping (S.S.) model.<sup>23</sup>

For relative energies higher than 5 eV,  $Q_{mp}$  levels off at a roughly constant value that is less negative than  $Q_{ss}$ . At high initial relative energies, therefore, the product  $NO^+$  is observed to have higher velocity than that predicted by S.S. This is accompanied by a reduction of the width of the product velocity distribution, and a reduction of the

total reaction cross-section. These trends have previously been observed<sup>24-29</sup> in reactions of the type:



and have been attributed to product dissociation.<sup>26-29</sup> A product ion formed with internal energy in excess of its dissociation energy is likely to decompose before it reaches the detector. Therefore, at high initial relative energy, only those ions with high translational (low internal) energy will be detected; the low velocity part of the product spectrum will be "eaten away" by dissociation, resulting in the observed forward shifting, narrowing of the distribution and overall reduction of cross-section.

From conservation of energy we can write:

$$T_f = T_i + I_i - I_f + \Delta E_o, \quad (6)$$

where  $I_i$  and  $I_f$  are initial and final internal energies and  $\Delta E_o$  is the exoergicity of the reaction. If we assume no product is observed for which  $I_f$  exceeds the dissociation energy  $D$ ,<sup>30</sup> we obtain a lower limit for  $Q$ :

$$Q \leq I_i + \Delta E_o - D. \quad (7)$$

For the present experimental conditions  $I_i$  can be taken to be about zero since thermal  $O_2$  is essentially entirely in the ground vibrational state, and, as argued previously, the primary beam is almost completely composed of ground state  $N^+(^3P)$  ions. The difference  $\Delta E_o - D$  for dissociation into the lowest energy fragments  $N(^4S^o) + O^+(^4S^o) + O(^3P)$  is found directly from spectroscopic data to be -4.15 eV. The horizontal solid line in figure 3 shows this lower limit for  $Q$ . The experimental peak value points all lie above this line, and are therefore qualitatively consistent with the dissociation hypothesis. In order to quantitatively test the hypothesis, however, we found it necessary to perform a fairly extensive kinematic analysis of the experimental data to properly take into account the effects of finite resolution.

### B. QUANTITATIVE

Briefly, the kinematic analysis is carried out in the following way. First, a "reaction model"  $P_T(u, \theta)$  is chosen which, with proper

choice of parameters, will adequately describe the product distribution as a function of center of mass velocity  $u$  and angle  $\Theta$ , that would result from collisions of a given initial relative energy  $T$ . To compare with experiment, this distribution should, rigorously, be integrated over the finite dimensions of the detection slit and scattering region as well as over the finite energy and angular spreads of the reactant beams. Under certain assumptions shown to be valid for this reaction the result of the integration over the finite acceptance angle of the slit and the finite volume of the scattering zone, can be approximated by a function  $G(\Theta)P_T(u, \Theta)$ .<sup>31</sup>  $G(\Theta)$  is a complicated function which depends largely upon dimensions of the detection slit and scattering region; i.e., it is characteristic of the particular experimental apparatus, and only weakly dependent upon the particular chemical reaction under investigation.<sup>32</sup> For this analysis,  $G(\Theta)$  was approximated by the function

$$G(\Theta) = \sinh^{-1} [h / (\sin^2 \Theta + w^2)^{1/2}], \quad (8)$$

where  $h$  and  $w$  are parameters which depend on the apparatus.<sup>31</sup>

The resulting function  $G(\Theta)P_T(u, \Theta)$  was integrated over the measured reactant beam angular and energy distributions by a procedure very similar to that described by Entemann.<sup>33</sup>

The reaction model  $P_T(u, \Theta)$  for this reaction was chosen to be of the following form:

$$P_T(u, \Theta) = \frac{1}{\sqrt{T}} \exp \left[ - \frac{(u - u_m)^2}{\Delta^2} \right], \quad (9a)$$

with

$$P_T(u, \Theta) = 0 \text{ if } T_f - T_i > \Delta E_0, \quad (9b)$$

and

$$P_T(u, \Theta) = 0 \text{ if } I_f > I_{\max} \quad (9c)$$

The reaction model defined by (9) describes a Gaussian product distribution about some arbitrary point  $u_m$  in velocity space.  $u_m$  is a vector whose coordinates in the center of mass system are given by  $u = u_m$  and  $\Theta = 0$ ; i.e., the model applies only to direct, forward scattered mechanisms. The factor  $1/\sqrt{T}$  simply weights the cross-section according to the Langevin energy

dependence. For the energies and energy spreads considered here, this factor was found to have a negligible effect.<sup>34</sup> Condition (9b) assures that the product cannot be given more energy than is consistent with the exoergicity of the reaction. Relaxing this condition resulted in a negligible change in these calculations. With inclusion of condition (9c), the reaction model attempts to describe eating away of product due to dissociation in the simplest possible way:  $P_T$  is set equal to zero if the product internal energy exceeds some value  $I_{\max}$ .

The model has three adjustable parameters, the most probable velocity  $u_m$ , the distribution width  $\Delta$ , and the maximum allowable internal energy  $I_{\max}$  (or more correctly, the quantity  $I_{\max} - \Delta E_0$ ). After many calculations with various values of the parameters, we found that reaction model (9) does quite accurately describe our experimental results, given the following choices of the parameters:

$$u_m = u_{ss} + .05 \pm .2 \times 10^5 \text{ cm/sec}, \quad (10a)$$

$$\Delta = 1.6 \times 10^5 \pm .3 \times 10^5 \text{ cm/sec}, \quad (10b)$$

and  $I_{\max} - \Delta E_0 = 4.2 \pm .2 \text{ eV}. \quad (10c)$

$u_{ss}$  is the velocity predicted by spectator stripping:

$$u_{ss} = \frac{M_N \cdot M_O}{M_{NO_2} \cdot M_{NO}} V_{rel} = .162 V_{rel} \quad (11)$$

These parameter values fit all experimental results over the entire range of energies studied.

Note that, while the best fit was obtained with  $u_m$  chosen slightly forward of the spectator stripping velocity, the error limits are such that within experimental error, the simple spectator stripping model does correctly predict the most probable product velocity.

The width of the product velocity distribution is found to be roughly independent of  $N^+$  energy. This is consistent with the feeling that the dominant factor in producing the finite spread of product velocities is the vibrational and rotational motion of the neutral  $O_2$  molecule. This picture would further suggest that the distribution be roughly symmetrical about its most probable value, which also appears to be born out by the experiments.



As mentioned above, the spectroscopic value of  $D_0(\text{NO}^+) - \Delta E_0$  for dissociation of  $\text{NO}^+$  into its lowest energy fragments,  $\text{O}^+(^4\text{S}^0) + \text{N}(^4\text{S}^0)$ , is 4.15 eV. For dissociation into the next lowest energy channel,  $\text{O}(^3\text{P}) + \text{N}^+(^3\text{P})$ , the spectroscopic value of  $D(\text{NO}^+) - \Delta E_0$  is 5.08 eV. From the close agreement of the former value with the experimental value (10c), and the fact that the latter value is well outside the error range given by (10c), we conclude that the  $\text{NO}^+$  formed by reaction (1) dissociates to  $\text{O}^+(^4\text{S}^0) + \text{N}(^4\text{S}^0)$ , not to  $\text{N}^+(^3\text{P}) + \text{O}(^3\text{P})$  or any other excited species. Inspection of the electronic correlation diagram for  $\text{NO}^+$  shows that of the energetically allowed products, only  $\text{NO}^+(^1\Sigma^+)$  and  $\text{NO}^+(^3\Sigma^+)$  dissociate adiabatically to this limit.<sup>35,36</sup> Furthermore, the fact that the  $\text{NO}^+$  dissociates as soon as the difference between total available energy and final translational energy exceeds the dissociation energy of  $\text{NO}^+$  indicates that all of the remaining energy goes into internal energy of  $\text{NO}^+$ . The atomic oxygen product must be formed in its ground state  $\text{O}(^3\text{P})$ . Little or no vibrational or rotational energy (maximum of about .25 eV) in excess of the dissociation energy of  $\text{NO}^+$  is required to cause it to decompose before reaching the detector.<sup>30</sup>

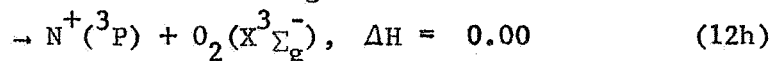
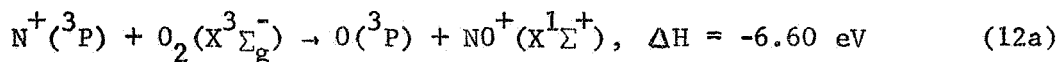
Figures 1a and 2a show the product distributions predicted by reaction model (9) for relative collision energies of 3.16 and 8.9 eV. The parameters were taken to be  $u_m = u_{ss}$ ,  $\Delta = 1.6 \times 10^5$  cm/sec, and  $I_{\text{max}} - \Delta E_0 = 4.15$  eV. The dashed circles delimit the area allowed by conditions (9b) and (9c). Figures 1b and 2b were obtained by integrating the distributions of figures 1a and 2a over velocity and angular spreads of the colliding beams which were measured for the corresponding experiments, 1c and 2c.

The model calculations, in general, predict a somewhat sharper product angular distribution than that observed. This is not surprising. For ion-molecule reactions the strong ion-induced dipole attraction, while usually not sufficient to produce much actual spiraling, is thought to cause considerable bending of trajectories.<sup>30,34</sup> This would suggest replacing the present spherical distribution model with one which predicts a weaker dependence on center of mass angle than on velocity. Aside from this small discrepancy between angular distributions, agreement between model calculations and experiments is excellent, as can be seen by comparing figures 1b and 2b with 1c and 2c.

The dashed line of figure 3 is a plot of  $Q_{mp}$  obtained from model calculations using typical reactant beam spreads and the same model parameters as figures 1 and 2. This line agrees quite well with experiment, within the scatter of points. In the absence of reactant beam spreads, the model would predict  $Q_{mp}$  to be that given by the solid line; i.e., spectator stripping at low energies, and  $Q_{mp} = -4.15$  eV. when dissociation becomes important. The deviation of the dashed line from the solid line is due entirely to resolution effects. It can be seen from figure 3 that this deviation is substantial, even though the experiments and computer simulations were performed with reactant beams of relatively narrow angular and energy spreads. In particular, an estimate of the threshold for product dissociation from the present experimental  $Q$ -value plot, without a kinematic analysis, could lead to an error of as much as 1 eV. We conclude that it is important that a careful kinematic analysis be undertaken before any quantitative conclusions are made from crossed-beam data.

#### IV DISCUSSION

12 a-i are the nine lowest energy channels for collision of  $N^+$  with  $O_2$ .<sup>38</sup>



$\Delta H$  for each reaction channel was obtained using the atomic energy levels and ionization potentials tabulated by Moore,<sup>39</sup> the electronic energy levels and dissociation energies of NO and  $O_2$  given by Herzberg,<sup>40</sup>

and the ionization thresholds of NO and O<sub>2</sub> reported by Al-Joboury and Turner,<sup>41</sup> and Edqvist, et. al.<sup>36</sup>

Five of the above channels result in formation of NO<sup>+</sup> product. However, the analysis of the preceding section shows that the NO<sup>+</sup> product must be either NO<sup>+</sup>(<sup>1</sup>Σ<sup>+</sup>) or NO<sup>+</sup>(<sup>3</sup>Σ<sup>+</sup>), and that the O product must be O(<sup>3</sup>P). Therefore only channels a and f can be possible important contributors to formation of NO<sup>+</sup> in this reaction. This is shown in Table I which gives the maximum value for which NO<sup>+</sup> dissociation could occur for each of the possible channels.

In figure 4 we have attempted to give a schematic picture of the correlation between the various reaction channels. For convenience, we have labeled the states of NO<sub>2</sub><sup>+</sup> according to the symmetry properties of their linear NOO<sup>+</sup> configurations. Except for the lowest state, the energy levels of NO<sub>2</sub><sup>+</sup> are not known.<sup>42</sup> Therefore, the positions and even the order of the states of NO<sub>2</sub><sup>+</sup> indicated by dashed lines in figure 4 are extremely uncertain. No quantitative estimate of their energies is intended.

We can nonetheless make some tentative conclusions from this correlation diagram. The initial channel, h, correlates adiabatically with reaction channel d, through a state labeled <sup>1</sup>Σ<sup>+</sup>. Since channel d is not observed, the reaction must occur by a non-adiabatic mechanism,<sup>43</sup> and from this and the large cross-sections of both reactions (1) and (2), this non-adiabatic transition must be very efficient.

The NO<sub>2</sub><sup>+</sup> state labeled <sup>3</sup>Π in figure 4 correlates with a and c, both of which are possible products. Relative to separated O(<sup>3</sup>P) and NO<sup>+</sup>(X<sup>1</sup>Σ<sup>+</sup>), it is expected to be repulsive by analogy with CO<sub>2</sub> and N<sub>2</sub>O.<sup>44,45</sup> It is not clear whether it is attractive or repulsive relative to separated N(<sup>4</sup>S<sup>o</sup>) and O<sub>2</sub><sup>+</sup>(X<sup>2</sup>Π<sub>g</sub>). In figure 4 it is drawn slightly attractive, and as such does not intersect the <sup>1</sup>Σ<sup>+</sup> state connecting h and d. If they do in fact intersect, then there is little chance of channel a playing an important part in reaction (1). If they do intersect it would still require a non-adiabatic transition between states of different spin multiplicity to produce channel c. The very small cross-section of the reaction O<sup>+</sup> + N<sub>2</sub> → NO<sup>+</sup> has been attributed to the fact that a non-adiabatic transition between states of different spin multiplicity is required for the reaction to proceed at very low energies, and that such a transition is unlikely.<sup>46-48</sup> Similarly, in

the present system it does not appear probable that the transition probability between the surface correlating with h and that correlating with a and c could be large enough to account for the observed cross-section.<sup>49</sup>

In any case, it seems likely that the state correlating with f and g is primarily involved. This surface is a singlet, so no spin transition would be involved, and from the known energies of the resulting products, it must cross the surface correlating with incoming channel h. Because of the near-degeneracy of the incoming channel and channel g, it is further likely that the surface crossing occurs at fairly large distances as the  $N^+$  and  $O_2$  approach. If this conjecture is correct, the reaction can be pictured as a two-step process: an electron jump at moderately large separation followed by a collision resulting either in  $O(^3P) + NO^+(^3\Sigma^+)$ , (reactive collision), or  $O_2^+(X^2\Pi_g) + N(^2D)$ , (no further reaction). Either channel, g or h, results in electronically excited product.

In the light of this discussion, it is not surprising that reaction (1) does not involve a long-lived collision complex.  $NO_2^+$  is known to be strongly bound in its ground electronic state, so there does exist a deep potential well that could possibly trap the interacting atoms. But a non-adiabatic transition from the incoming channel to the lowest surface appears very improbable, since no crossing or avoided crossing exists. This is indicated experimentally by the apparent absence of channel b, which might be expected to be a major product of decomposition of  $NO_2^+(X^1\Sigma^+)$ .

It is not unreasonable to expect that there might be a strong correlation between the exothermicity of a reaction and the resulting product translational energy. In fact, Franklin and Haney have observed such a correlation in ion-molecule reactions involving transfer of a hydrogenic species.<sup>50</sup> For this correlation to be valid for the present system, the large exothermicity (6.60eV) of reaction (1) would require that the product translational energy be far greater than that predicted by spectator stripping. The fact that the observed product translational energy is close to that predicted by spectator stripping is consistent with the proposed formation of electronically excited  $NO^+(^3\Sigma^+)$ , thereby using up 6.31 eV,<sup>36</sup> most of the excess energy supplied by the exothermicity.<sup>51</sup>

As discussed earlier, none of the simple models of direct reactions take into account the detailed nature of the chemical forces involved, and as a result are useful only when the short-range effects are "normal" or unimportant. Reaction (1), for which we propose an electron-jump mechanism, lies outside the scope of these models. In particular, the polarization-stripping model (ref. 12) could easily be extended to systems which deviate from ion-induced dipole forces, provided that a reasonable long-range form of the potential could be estimated, and, in addition that this estimate be at least approximately valid at the reaction radius  $r_0$ . For the present system, however, the fact that the reaction does not proceed on a single adiabatic potential surface makes it very difficult to estimate the necessary potentials. Without such estimates, the polarization-stripping model cannot be applied in a meaningful way.

The apparent agreement of our results with one aspect of the spectator stripping picture, i.e., its accurate prediction of the most probable product velocity, should also not be taken seriously. There are several other reaction models which, though differing considerably from the spectator stripping picture on the microscopic mechanistic level, still result in very similar macroscopic predictions. For example, the hard sphere model proposed by Suplinskas<sup>14</sup> is conceptually very different from spectator stripping. Yet a recent application of the hard sphere model to the  $\text{Ar}^+ - \text{D}_2$  system<sup>15</sup> has resulted in a predicted most probable  $\text{ArD}^+$  product velocity that is almost exactly equal to the spectator stripping prediction. It would be dangerous, therefore, to make any conclusion from the present experiment about the validity of the basic assumption of the spectator stripping model.

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FOOTNOTES

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FOOTNOTES (Cont'd.)

19. Producing  $N^+$  ions by reaction (4) had the disadvantage of higher background pressures in collision chamber, but the resulting beam could be focused to a lower energy with a narrower spread than that produced by electron impact of  $N_2O$ .
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38. Channels 12a-i do not include the possibility of forming stable  $NO_2^+$ , which would require emission of light or presence of a third body.<sup>2</sup>



FOOTNOTES (Cont'd.)

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43. The initial channel h can also correlate adiabatically with channel f through a  ${}^5\Pi$  state. We would expect this state to be repulsive so that if this route were important, the reaction would exhibit an apparent activation energy. This is consistent with the small cross-section and observed energy dependence of reaction 3 (see references 4 and 11).
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49. Reaction (4), for which channel c is the initial channel, might provide an additional clue to the shape of the  ${}^3\Pi^-(a-g)$  surface. This reaction has a thermal rate constant of  $1.8 \times 10^{-10}$  cm<sup>3</sup>/sec.<sup>4</sup> This is much larger than rate constants observed for reactions which must overcome strongly repulsive potentials such as reaction (3)<sup>4</sup> or the  $\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$  reaction (see ref. 47). However, it is still much smaller than the rate constants observed for ordinary ion-molecule reactions involving strong attractive ion-induced dipole potentials. Measurements of the energy dependence of reaction (4) to determine if it has an effective activation energy would be very useful in this connection, but it appears that the effective potential involved is neither strongly repulsive nor strongly attractive.
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51. The observed moderate translational energy of the products is the only experimental indication that f rather than a might be the primary reaction channel. Therefore this conclusion is to be considered only speculative. An attempt to observe  $\text{NO}^+({}^3\Sigma^+) \rightarrow \text{NO}^+({}^1\Sigma^+)$  radiation from the products of reaction (1) might be an informative experiment.

TABLE I.

The maximum Q value,  $Q_{\text{dissoc}}$ , for which  $\text{NO}^+$  dissociation can occur.

Channel	$\text{NO}^+$	0	$\Delta E_0$	-D	$Q_{\text{dissoc}}$
a	$1_{\Sigma}^+$	$3_P$	6.60 eV	-10.75 eV	-4.15 eV
f	$3_{\Sigma}^+$	$3_P$	0.29	- 4.44	-4.15
i	$3_{\Pi}$	$3_P$	-0.62	- 4.46	-5.08
b	$1_{\Sigma}^+$	$1_D$	4.63	-10.75	-6.12
d	$1_{\Sigma}^+$	$1_S$	2.41	-10.75	-8.34

FIGURE CAPTIONS

Figure 1. Newton diagrams showing the relative intensity of  $\text{NO}^+$  product from  $\text{N}^+ + \text{O}_2$  with relative energy of 3.17 eV. a. Two dimensional distribution predicted by the reaction model given by Eq. 9. b. Distribution in a plane of finite thickness defined by sources and detector. This results from multiplying distribution a) by  $G(\Theta)$  (causing narrowing), and taking into account experimental initial beam spreads. c. Experimental product distribution.

Figure 2. Newton diagrams for initial  $\text{N}^+ - \text{O}_2$  relative energy of 8.29 eV., obtained in the same way as Fig. 1.

Figure 3. Most probable Q values as a function of initial relative energy. The circles are experimental points. The solid line assumes spectator stripping for low initial energies, and for higher initial energies,  $Q = -4.15$  eV (the value of  $\Delta E_0 - D$  for  $\text{NO}^+$  dissociation into its lowest energy fragments). The dashed line is the  $Q_{\text{mp}}$  plotted against the most probable collision energy. It is calculated assuming the spectator-stripping, dissociation at  $Q = -4.15$  eV model, but taking into account typical experimental beam spreads.

Figure 4. Tentative electronic correlation diagram for  $\text{NO}_2^+$ . States are labeled according to their linear  $\text{NOO}^+$  designations. Caution: The diagram is quantitatively extremely uncertain.

Fig 1

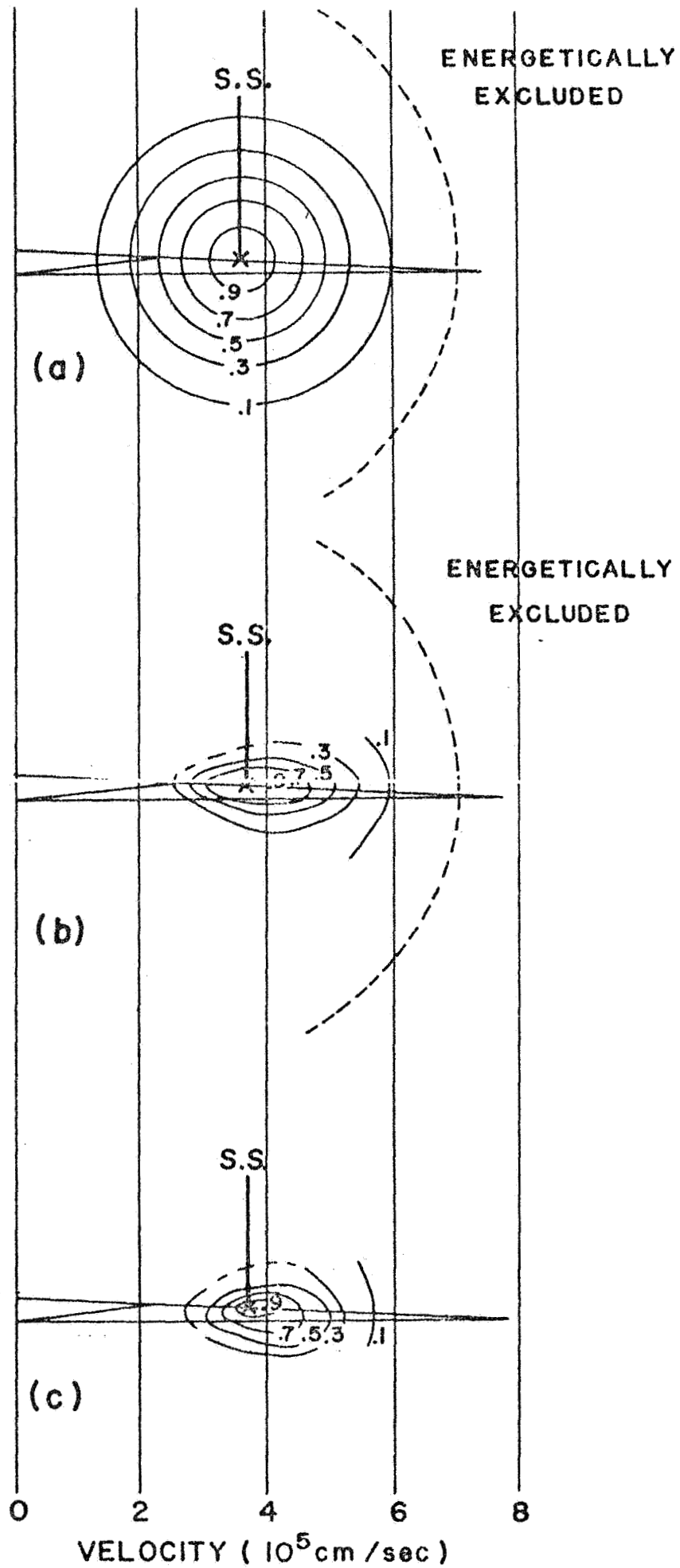
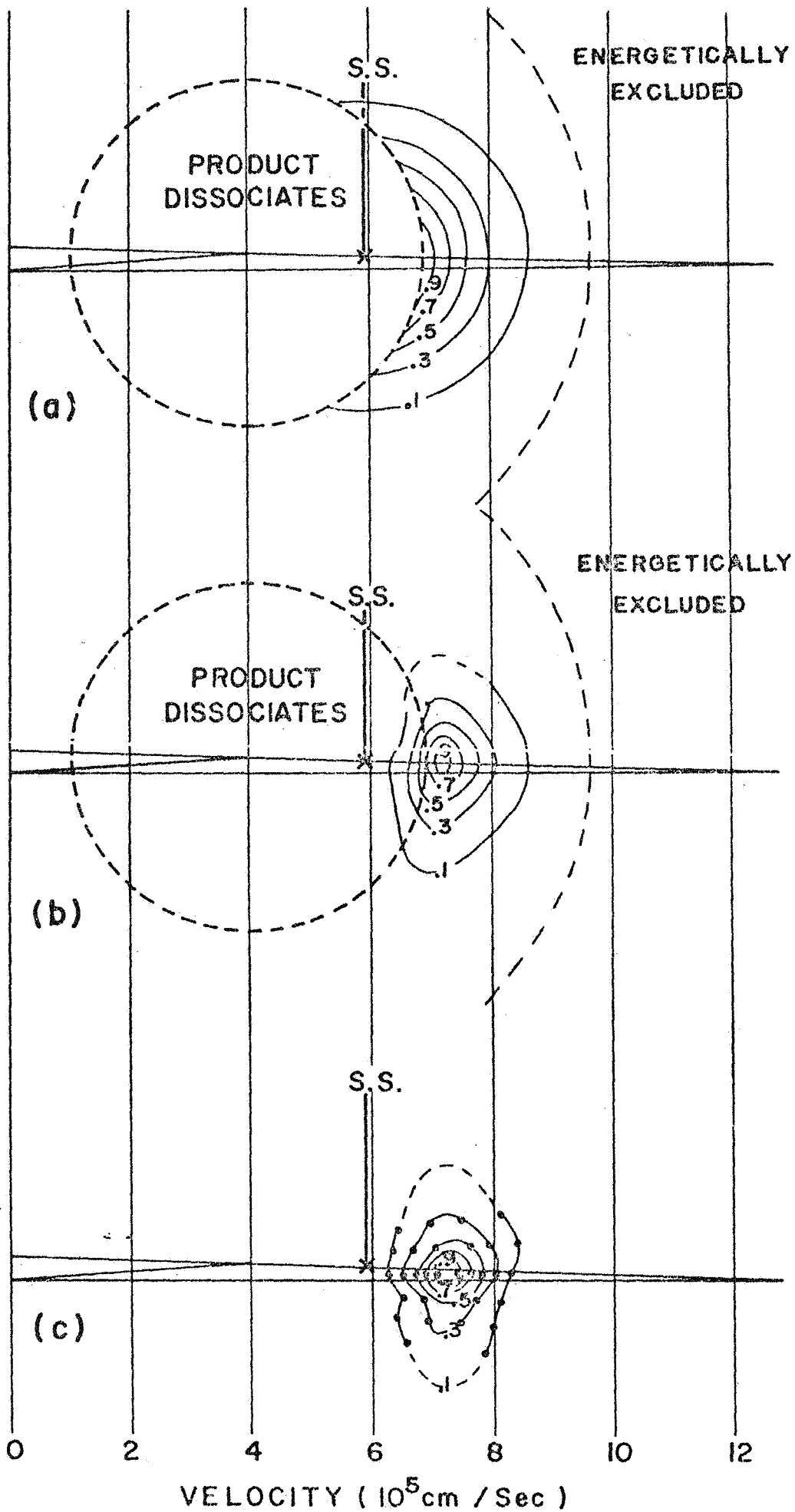


Fig 2



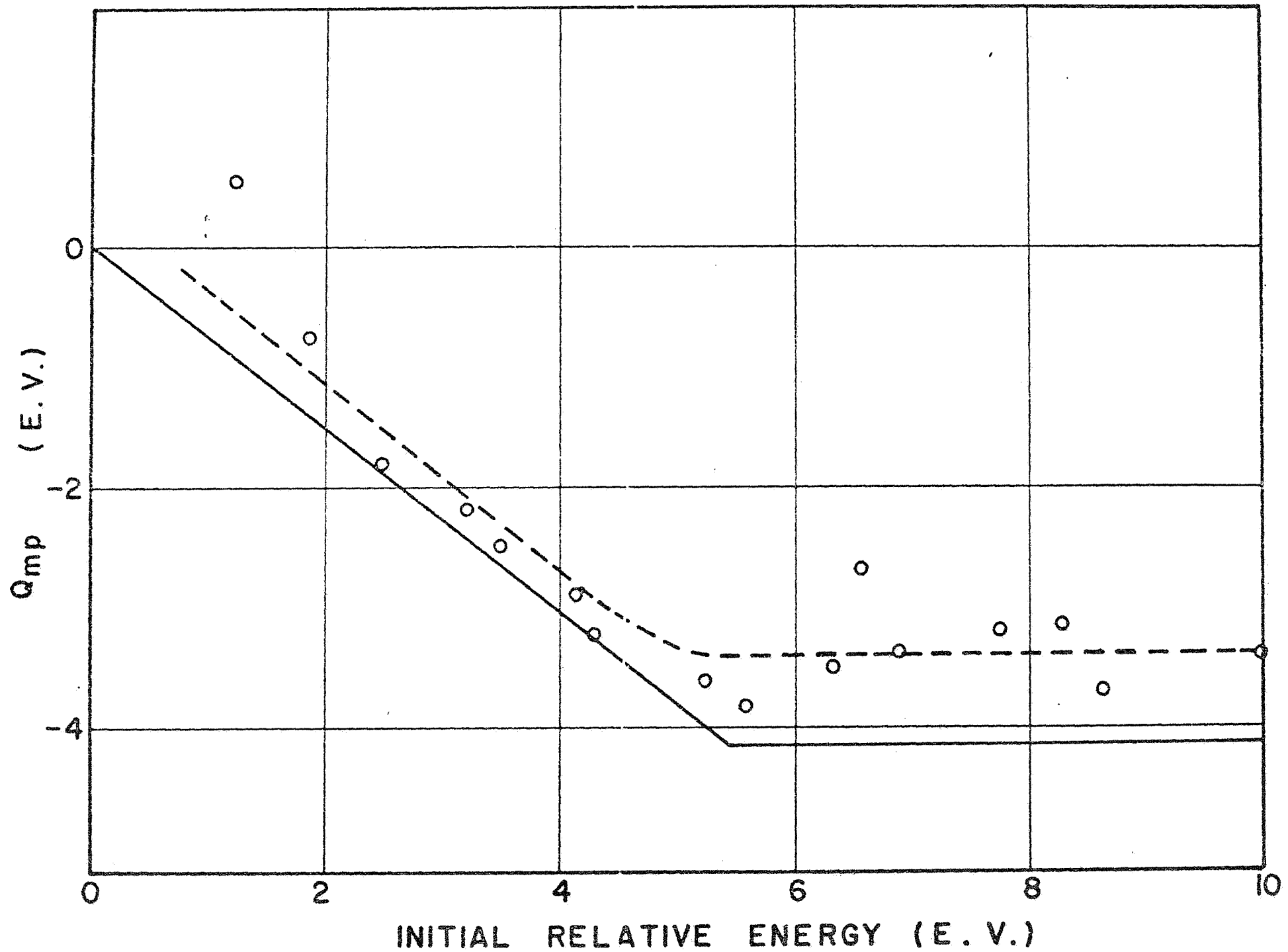


Fig 3

