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A CROSSED BEAM STUDY OF THE REACTION

$N^+ + O_2 \rightarrow NO^+ + O$

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ABSTRACT

The reaction $N^+ + O_2 \rightarrow NO^+ + O$ 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 NO_2^+. This is not the case for previously well-studied ion-molecule reactions (e.g., $Ar^+ + D_2$), the dynamics of which are closely represented by simple models dominated by long-range electrostatic forces (e.g. "polarization-stripping").

Beams of N^+ in the ground (^3P) state were crossed with thermal O_2 beams and the angular and velocity distributions of the 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 $O(^3P)$ and a state of NO^+ which, with excess energy, dissociates to $N(^4S^o)$ and $O^+(^4S^o)$. Consideration of the correlation diagram for NO_2^+ then indicates the following mechanism as probable: At moderately large separation $N^+(^3P)$ and $O_2(^3\Sigma_g^-)$, originally on a surface correlating with linear NO_2^+ (excited $^1\Sigma^+$), experience an electron jump leading to a surface correlating similarly with $NO_2^+(^1\Sigma^-$ or $^1\pi)$. Upon closer approach an O atom is transferred leading adiabatically to $O(^3P) + NO^+(^3\Sigma^+)$. (The latter will dissociate to $N(^4S^o)$ and $O^+(^4S^o)$ 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.

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.[1] 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.[1] The primary N^+ loss mechanism is reaction with O_2.[1]

Because of this atmospheric importance the reactions

$$N^+ + O_2 \rightarrow NO^+ + O \qquad (1)$$

and

$$N^+ + O_2 \rightarrow O_2^+ + N \qquad (2)$$

have been the subject of extensive study.[2-10] The related reactions

$$O^+ + NO \rightarrow NO^+ + O \qquad (3)$$

and

$$N + O_2^+ \rightarrow NO^+ + O \qquad (4)$$

have also been experimentally investigated.[4,11] 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"[12, 13] and the "kinematic"[14, 15] 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 NO^+ product when its internal energy is just sufficient for it to dissociate to its ground state fragments. From knowledge of the NO^+ electronic states, it can be seen that this requires that the 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 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 $NO^+(^3\Sigma^+)$.

I. EXPERIMENTAL

Experiments were performed with the crossed-beam apparatus EVA[12]. The experiments proceed basically as follows: N^+ ions are formed by either of the two methods described below, mass analyzed in a 180° 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° by a modulated, thermal beam of oxygen (temperature about 55° C). Ions from the collision zone pass through a detection slit, a stopping-potential energy analyzer and a 60° sector mass spectrometer before being detected by an electron multiplier. Phase sensitive detection of the 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.[16]

N^+ ions were produced by two methods. The first was from N_2O by impact of 120 Volt electrons. Such a beam should contain 90% $N^+(^3P)$ and about 10% $N^+(^1S)$, according to Lindholm's data.[17] The second was by 120 V. electron impact of a mixture of He and N_2 ($P(He)/P(N_2) \simeq 20$) at relatively high pressures. This method makes use of the very fast reaction[18]

$$He^{+}(^{2}S) + N_{2}(X^{1}\Sigma g^{+}) \rightarrow He(^{1}S) + N(^{4}S) + N^{+}(^{3}P), \Delta H=0.28 \text{ e.V.} \qquad (5)$$

Since formation of the first excited ^{4}S state of N^{+} by this reaction is 1.62 eV endothermic, we can be sure that all 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 He/N_2 gaseous mixture was ionized at lower pressures (about 10^{-4} Torr in the ionization chamber), the energy spectrum of N^{+} produced was several eV broad. This corresponds to N^{+} (and perhaps some N_2^{++}) formed directly by electron impact. However, when the pressure was increased a peak of lower energy and narrower spread appeared, due to N^{+} formed by the charge transfer between He^{+} and N_2. At optimum conditions (ionization chamber pressure about 10^{-2}Torr) the broad N^{+} distribution was negligible in comparison with the N^{+} peak formed by charge exchange.

There was no observable difference in experimental results when N^{+} ions were produced by electron impact of N_2O rather than by reaction (4). Therefore, we conclude that most of the 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 $N^{+}(^{3}P)$ beams with energies down to 1.8 eV could be obtained by either method.[19] Commercial grade bottled N_2, N_2O, He and O_2 were used for these experiments.

II. RESULTS

Energy and angular distributions of 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.[20] Contour lines are constructed to represent the relative intensity of the 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 distribution is then converted to the cartesian system by dividing by V^2.[21] 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.).[22] 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.[23]

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[24-29] in reactions of the type:

$$X^+ + H_2 \rightarrow XH^+ + H, \ X^+ = Ar^+, N_2^+ \text{ or } CO^+,$$

and have been attributed to product dissociation.[26-29] 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:

$$T_f = T_i + I_i - I_f + \Delta E_o, \tag{6}$$

where I_i and I_f are initial and final internal energies and ΔE_o is the exoergicity of the reaction. If we assume no product is observed for which I_f exceeds the dissociation energy D,[30] we obtain a lower limit for Q:

$$Q \leq I_i + \Delta E_o - D. \tag{7}$$

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 ΔE_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 Θ, 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 $G(\Theta)P_T(u,\Theta)$.[31] $G(\Theta)$ 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.[32] For this analysis, $G(\Theta)$ was approximated by the function

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

where h and w are parameters which depend on the apparatus.[31]

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.[33]

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

$$P_T(u,\Theta) = \frac{1}{\sqrt{T}} \exp[-(\underset{\sim}{u} - \underset{\sim}{u}_m)^2/\Delta^2], \qquad (9a)$$

with

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

and

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

The reaction model defined by (9) describes a Gaussian product distribution about some arbitrary point $\underset{\sim}{u}_m$ in velocity space. $\underset{\sim}{u}_m$ 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.[34] 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 Δ, and the maximum allowable internal energy I_{max} (or more correctly, the quantity $I_{max} - \Delta E_o$). 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:

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

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

and

$$I_{max} - \Delta E_o = 4.2 \pm .2 \text{ eV}. \tag{10c}$$

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

$$u_{ss} = \frac{M_N \cdot M_O}{M_{NO_2} \cdot M_{NO}} V_{rel} = .162 \, V_{rel} \tag{11}$$

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 $D_o(NO^+)$ - ΔE_o for dissociation of NO^+ into its lowest energy fragments, $O^+(^4S^o)$ + $N(^4S^o)$, is 4.15 eV. For dissociation into the next lowest energy channel, $O(^3P) + N^+(^3P)$, the spectroscopic value of $D(NO^+)$ $-\Delta E_o$ 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 NO^+ formed by reaction (1) dissociates to $O^+(^4S^o) + N(^4S^o)$, not to $N^+(^3P) + O(^3P)$ or any other excited species. Inspection of the electronic correlation diagram for NO^+ shows that of the energetically allowed products, only $NO^+(^1\Sigma^+)$ and $NO^+(^3\Sigma^+)$ dissociate adiabatically to this limit.[35,36] Furthermore, the fact that the NO^+ dissociates as soon as the difference between total available energy and final translational energy exceeds the dissociation energy of NO^+ indicates that all of the remaining energy goes into internal energy of NO^+. The atomic oxygen product must be formed in its ground state $O(^3P)$. Little or no vibrational or rotational energy (maximum of about .25 eV) in excess of the dissociation energy of NO^+ is required to cause it to decompose before reaching the detector.[30]

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_{max} - ΔE_o = 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.[30,34] 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.[38]

$$
\begin{aligned}
N^+(^3P) + O_2(X^3\Sigma_g^-) &\rightarrow O(^3P) + NO^+(X^1\Sigma^+), & \Delta H &= -6.60 \text{ eV} && \text{(12a)}\\
&\rightarrow O(^1D) + NO^+(X^1\Sigma^+), & \Delta H &= -4.63 && \text{(12b)}\\
&\rightarrow N(^4S^o) + O_2{}^+(X^2\Pi_g), & \Delta H &= -2.47 && \text{(12c)}\\
&\rightarrow O(^1S) + NO^+(X^1\Sigma^+), & \Delta H &= -2.41 && \text{(12d)}\\
&\rightarrow O^+(^4S^o) + NO(X^2\Pi), & \Delta H &= -2.32 && \text{(12e)}\\
&\rightarrow O(^3P) + NO^+(^3\Sigma^+), & \Delta H &= -0.29 && \text{(12f)}\\
&\rightarrow N(^2D^o) + O_2{}^+(X^2\Pi_g), & \Delta H &= -0.09 && \text{(12g)}\\
&\rightarrow N^+(^3P) + O_2(X^3\Sigma_g^-), & \Delta H &= \ \ 0.00 && \text{(12h)}\\
&\rightarrow O(^3P) + NO^+(^3\Pi), & \Delta H &= \ \ 0.62 && \text{(12i)}
\end{aligned}
$$

ΔH for each reaction channel was obtained using the atomic energy levels and ionization potentials tabulated by Moore,[39] the electronic energy levels and dissociation energies of NO and O_2 given by Herzberg,[40] and the ionization thresholds of NO and O_2 reported by Al-Joboury and Turner,[41] and Edqvist, et. al.[36]

Five of the above channels result in formation of NO^+ product. However, the analysis of the preceding section shows that the NO^+ product must be either $NO^+(^1\Sigma^+)$ or $NO^+(^3\Sigma^+)$, and that the O product must be $O(^3P)$. Therefore only channels a and f can be possible important contributors to formation of NO^+ in this reaction. This is shown in Table I which gives the maximum value for which NO^+ 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_2^+ according to the symmetry properties of their linear NOO^+ configurations. Except for the lowest state, the energy levels of NO_2^+ are not known.[42] Therefore, the positions and even the order of the states of NO_2^+ 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 $^1\Sigma^+$. Since channel d is not observed, the reaction must occur by a non-adiabatic mechanism,[43] and from this and the large cross-sections of both reactions (1) and (2), this non-adiabatic transition must be very efficient.

The NO_2^+ state labeled $^3\Pi$ in figure 4 correlates with a and c, both of which are possible products. Relative to separated $O(^3P)$ and $NO^+(X^1\Sigma^+)$, it is expected to be repulsive by analogy with CO_2 and N_2O.[44,45] It is not clear whether it is attractive or repulsive relative to separated $N(^4S^o)$ and $O_2^+(X^2\Pi_g)$. In figure 4 it is drawn slightly attractive, and as such does not intersect the $^1\Sigma^+$ 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 $O^+ + N_2 \rightarrow NO^+$ 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.[46-48] 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.[49]

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.[50] 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,[36] most of the excess energy supplied by the exothermicity.[51]

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[14] is conceptually very different from spectator stripping. Yet a recent application of the hard sphere model to the Ar^+ - D_2 system[15] has resulted in a predicted most probable ArD^+ product velocity that it 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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1. The chemistry of N^+ in the upper atmosphere is discussed by M. B. McElroy, Planet. Space Sci. 15, 457 (1967).
2. W. L. Fite, J.A. Rutherford, W. F. Snow and V. A. J. Van Lint, Disc. Faraday Soc. 33, 264 (1962).
3. F. C. Fehsenfeld, A. L. Schmeltekopf and E. E. Ferguson, Planetary Space Sci. 13, 219 (1965).
4. P. D. Goldan, A. L. Schmeltekopf, F. C. Fehsenfeld, H. I. Schiff and E. E. Ferguson, J. Chem. Phys. 44, 4095 (1966).
5. R. F. Stebbing, B. R. Turner and J. A. Rutherford, J. Geophys. Res. 71, 771 (1966).
6. V. Aquilanti and G. G. Volpi, Ric. Sci. 36, 359 (1966).
7. P. Warneck, J. Geophys. Res. 72, 1651 (1967).
   P. Warneck, Planetary Space Sci. 15, 1349 (1967).
8. D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf and E. E. Ferguson, J. Chem., Phys. 49, 1365 (1968).
9. R. Johnsen, H. L. Brown and M. A. Biondi, J. Chem. Phys. 52, 5080 (1970).
10. R. F. Potter, J. Chem. Phys. 22, 974 (1954).
11. B. R. Turner, J. A. Rutherford and R. F. Stebbings, J. Geophys. Res. 71, 4521 (1966).
12. Z. Herman, J. Kerstetter, T. Rose and R. Wolfgang, Disc. Faraday Soc. 44, 123 (1967).
13. P. Hierl, Z. Herman and R. Wolfgang, J. Chem. Phys. 53, 660 (1970).
14. R. J. Suplinskas, J. Chem. Phys. 49, 5046 (1968).
15. T. F. George and R. Suplinskas, J. Chem. Phys., to be published.
16. Z. Herman, J. Kerstetter, T. Rose and R. Wolfgang, Revs. Sci. Instr. 40, 538 (1969).
17. A. Lindholm, Advan. in Chemistry Series, No. 58, American Chem. Soc., Washington, D.C., 1966, p. 1.
18. This method was suggested to us by E. E. Ferguson, private communication. For details, see reference 46 and papers quoted therein.

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.

20. D. R. Herschbach, Adv. Chem. Phys. 10, 332 (1966).

21. R. Wolfgang and R. J. Cross, Jr., J. Phys. Chem. 73, 743 (1969).

22. R. Wolfgang, Accts. of Chem. Res. 3, 48 (1970).

23. A. Henglein, K. Lacmann and G. Jacobs, Ber. Bunsenges. Physik. Chem. 69, 279 (1965).

24. K. Lacmann and A. Henglein, Ber. Bunsenges. Phys. Chem. 69, 292 (1965).

25. L. D. Doverspike, R. L. Champion and T. L. Bailey, J. Chem. Phys. 45, 4385 (1966).

26. W. R. Gentry, E. A. Gislason, Y. Lee, B. H. Mahan, and C. Tsao, Disc. Faraday Soc. 44, 137 (1967).

27. L. D. Doverspike and R. L. Champion, J. Chem. Phys. 46, 4718 (1967).

28. W. R. Gentry, E. A. Gislason, B. H. Mahan and C. Tsao, J. Chem. Phys. 49, 3058 (1968).

29. A. Henglein, "Molecular Beams and Reaction Kinetics," International School of Physics "Enrico Fermi" XLIV Course, 1968.

30. In the present experiment it requires from a x 10^{-5} to 2 x 10^{-4} seconds for ions to travel from the collision region through the mass spectrometer.

31. J. C. Tully, to be published.

32. In the limit of point collision region, point detector slit and zero initial rotational energy, $G(\Theta)$ reduces to $1/\sin\Theta$.

33. E. A. Entemann, Ph. D. Thesis, Harvard University (1967).

34. The reaction model was chosen to describe relative cross-sections as a function of product angle and velocity. No attempt was made to compare total reaction cross-sections.

35. F. R. Gilmore, J. Quant. Spectr. Radiative Transfer 5, 369 (1965).

36. O. Edqvist, E. Lindholm, L. E. Selin, H. Sjögren and L. Åsbrink, Arkiv för Fysik 40, 439 (1970).

37. D. T. Chang and J. C. Light, J. Chem. Phys. 52, 5687 (1970).

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.

FOOTNOTES (Cont'd.)

39. C. E. Moore, "Atomic Energy Levels," Vol. I, NBS Circular 467 (1949).

40. G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., Van Nostrand, Princeton (1950).

41. D. W. Turner and D. P. May, J. Chem. Phys. 45, 471 (1966).
M. I. Al-Joboury, D. P. May and D. W. Turner, J. Chem. Soc. 616 (1965).

42. A recent experimental and theoretical investigation of the electronic states of NO_2^+ has been reported by C. R. Brundle, D. Neumann, W. C. Price, D. Evans, A. W. Potts and D. G. Streets, J. Chem. Phys. 53, 705 (1970).

43. The initial channel h can also correlate adiabatically with channel f through a $^3\Pi$ 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).

44. G. Herzberg, "Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, 1967.

45. A. D. Walsh, J. Chem. Soc. 2266 (1953).

46. C. F. Giese, Advan. in Chemistry 58, 20 (1966).

47. E. E. Ferguson, Advan. in Electronics and Electron Physics 24, 1 (1968).

48. J. J. Kaufman and W. S. Koski, J. Chem. Phys. 50, 1942 (1969).

49. Reaction (4), for which channel c is the initial channel, might provide an additional clue to the shape of the $^3\Pi$ (a-c) surface. This reaction has a thermal rate constant of 1.8×10^{-10} $cm^3/sec.$[4] This is much larger than rate constants observed for reactions which must overcome strongly repulsive potentials such as reaction (3)[4] or the $O^+ + N_2 \rightarrow NO^+ + N$ 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.

50. J. L. Franklin and M. A. Haney, J. Phys. Chem. 73, 2857 (1969).

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 $NO^+(^3\Sigma^+) \rightarrow NO^+(^1\Sigma^+)$ radiation from the products of reaction (1) might be an informative experiment.

TABLE I.

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

Channel	NO^+	O	ΔE_o	-D	Q_{dissoc}
a	$^1\Sigma^+$	^3P	6.60 eV	-10.75 eV	-4.15 eV
f	$^3\Sigma^+$	^3P	0.29	- 4.44	-4.15
i	$^3\Pi$	^3P	-0.62	- 4.46	-5.08
b	$^1\Sigma^+$	^1D	4.63	-10.75	-6.12
d	$^1\Sigma^+$	^1S	2.41	-10.75	-8.34

FIGURE CAPTIONS

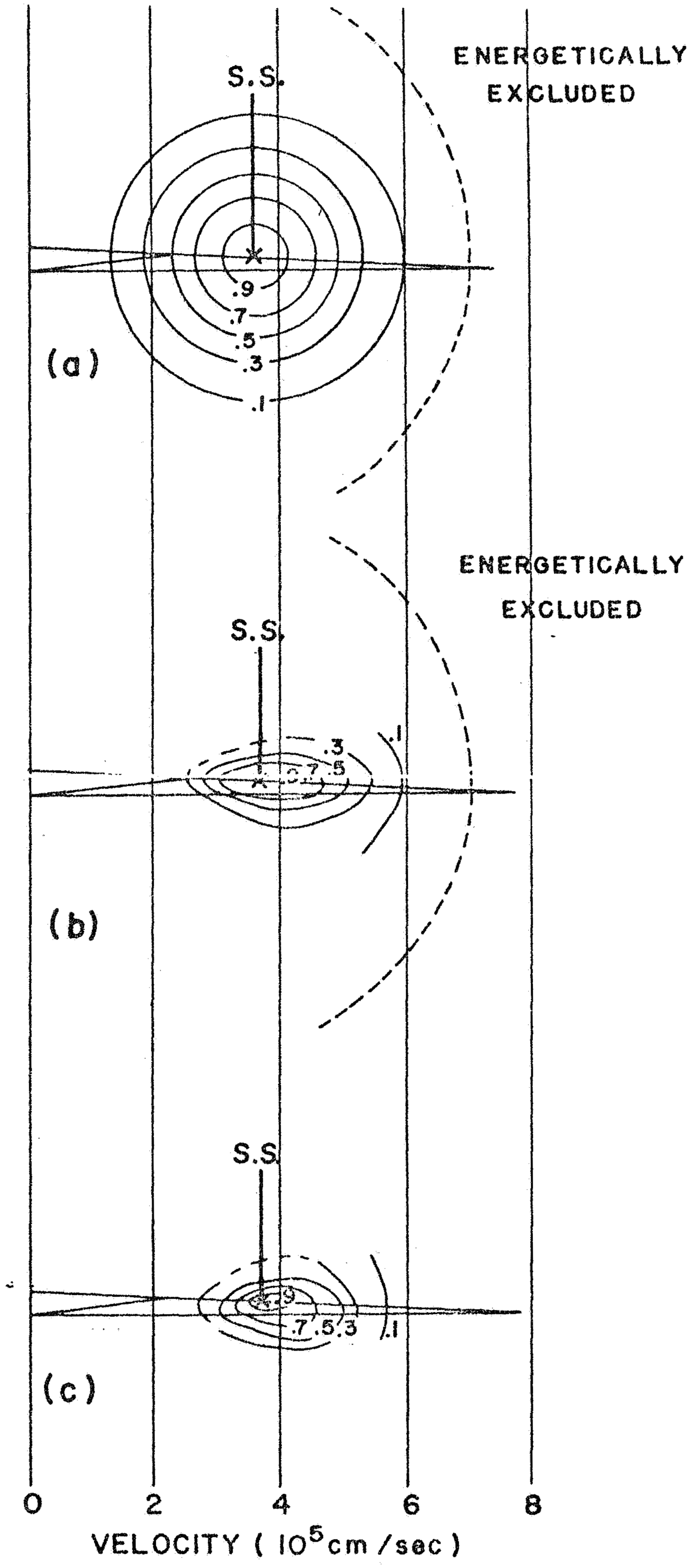
Figure 1. Newton diagrams showing the relative intensity of NO^+ product from $N^+ + O_2$ with relative energy of 3.17 eV. a. Two dimensional distribution predicted by the reaction model given by Eq. 9. b. Distribution in a plane of finite thickness defined by sources and detector. This results from 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 $N^+ - O_2$ 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 $\Delta E_o - D$ for NO^+ dissociation into its lowest energy fragments). The dashed line is the Q_{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 NO_2^+. States are labeled according to their linear NOO^+ designations. Caution: The diagram is quantitatively extremely uncertain.

Fig 1


ENERGETICALLY EXCLUDED
S.S.
.9
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.5
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(a)
ENERGETICALLY EXCLUDED
S.S.
.3
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(b)
S.S.
.9
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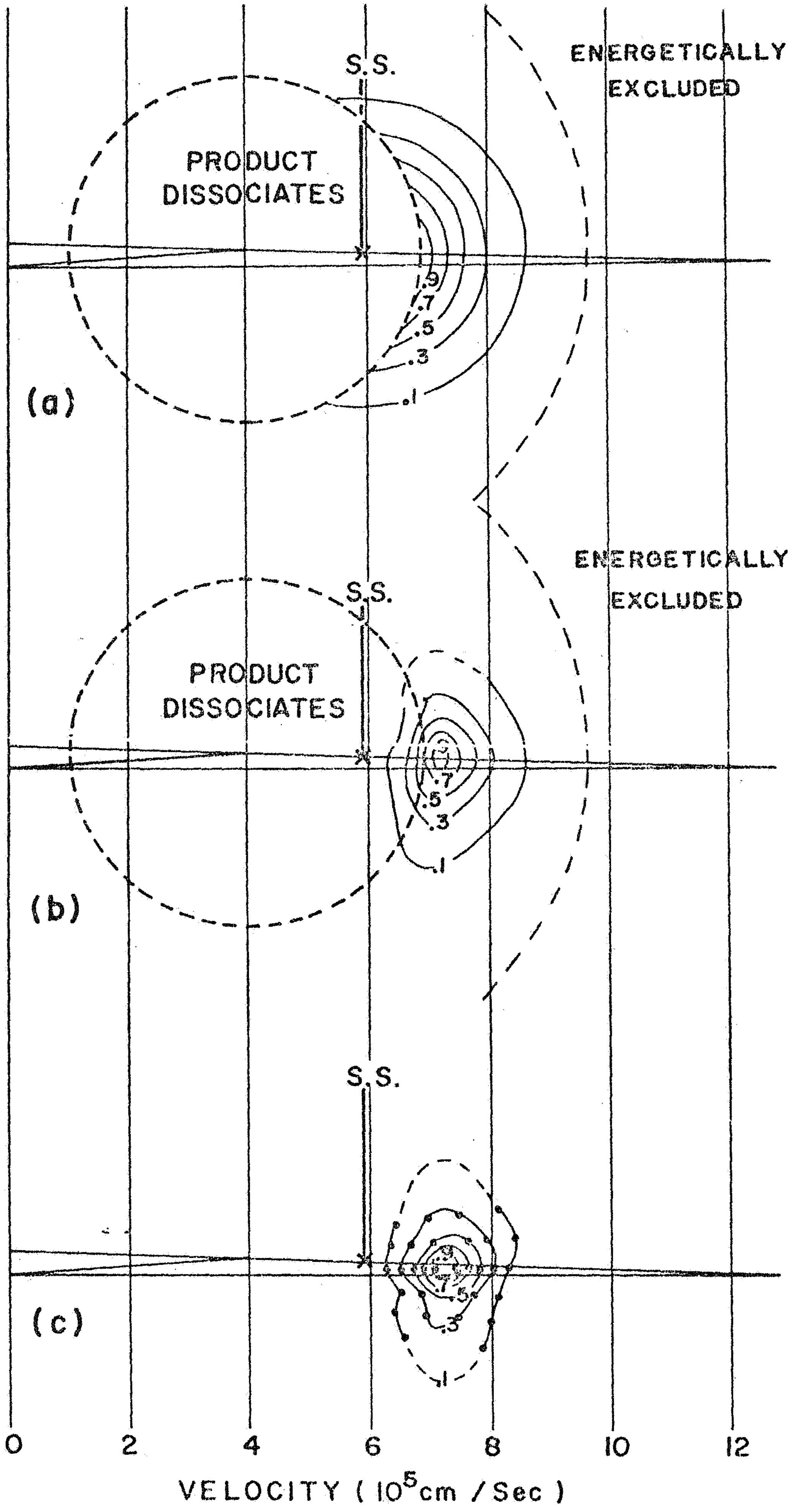
(c)
0
2
4
6
8
VELOCITY (10^5cm /sec)

Fig 2



ENERGETICALLY EXCLUDED
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PRODUCT DISSOCIATES
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12
VELOCITY (10^5cm / Sec)

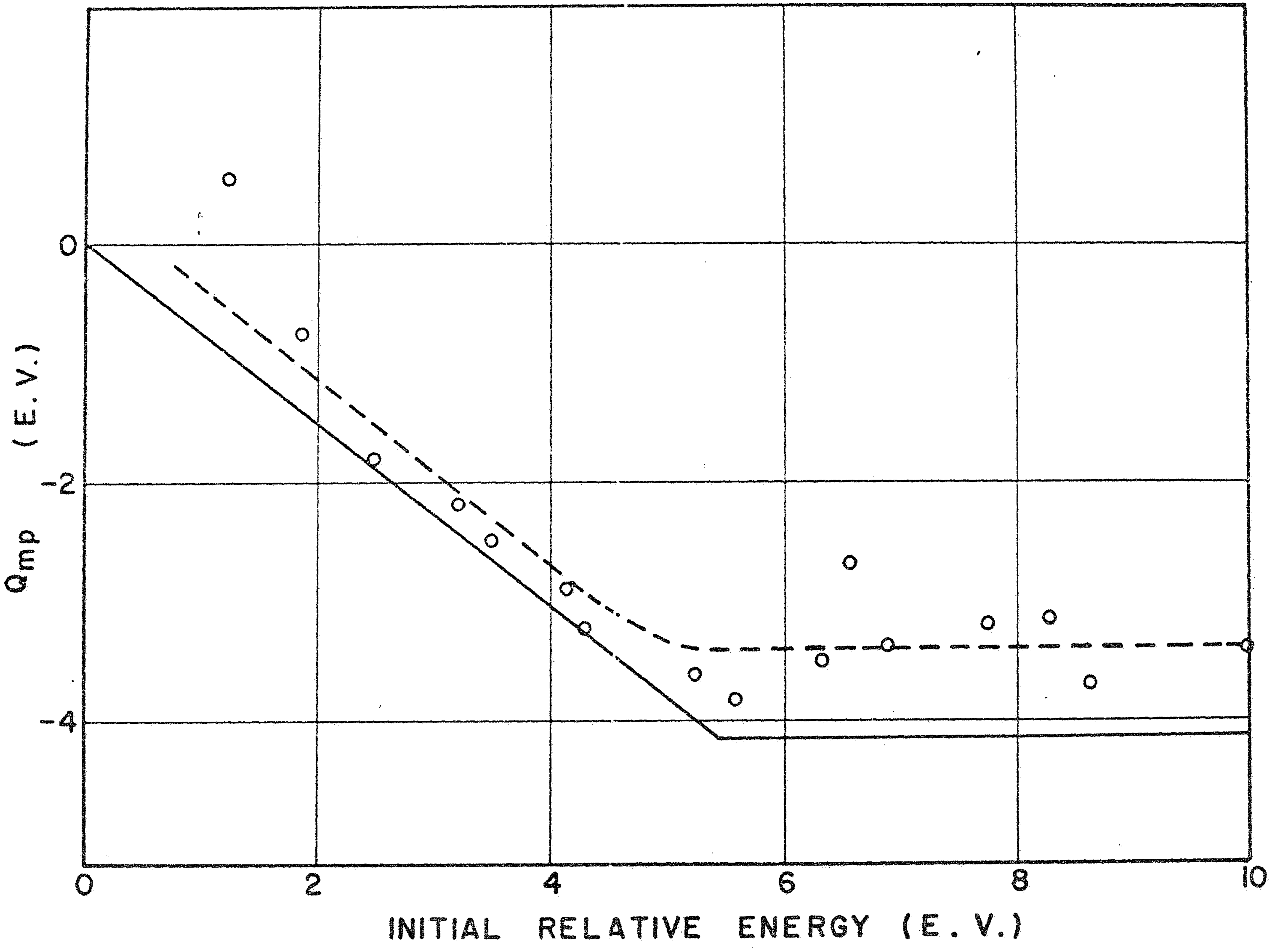
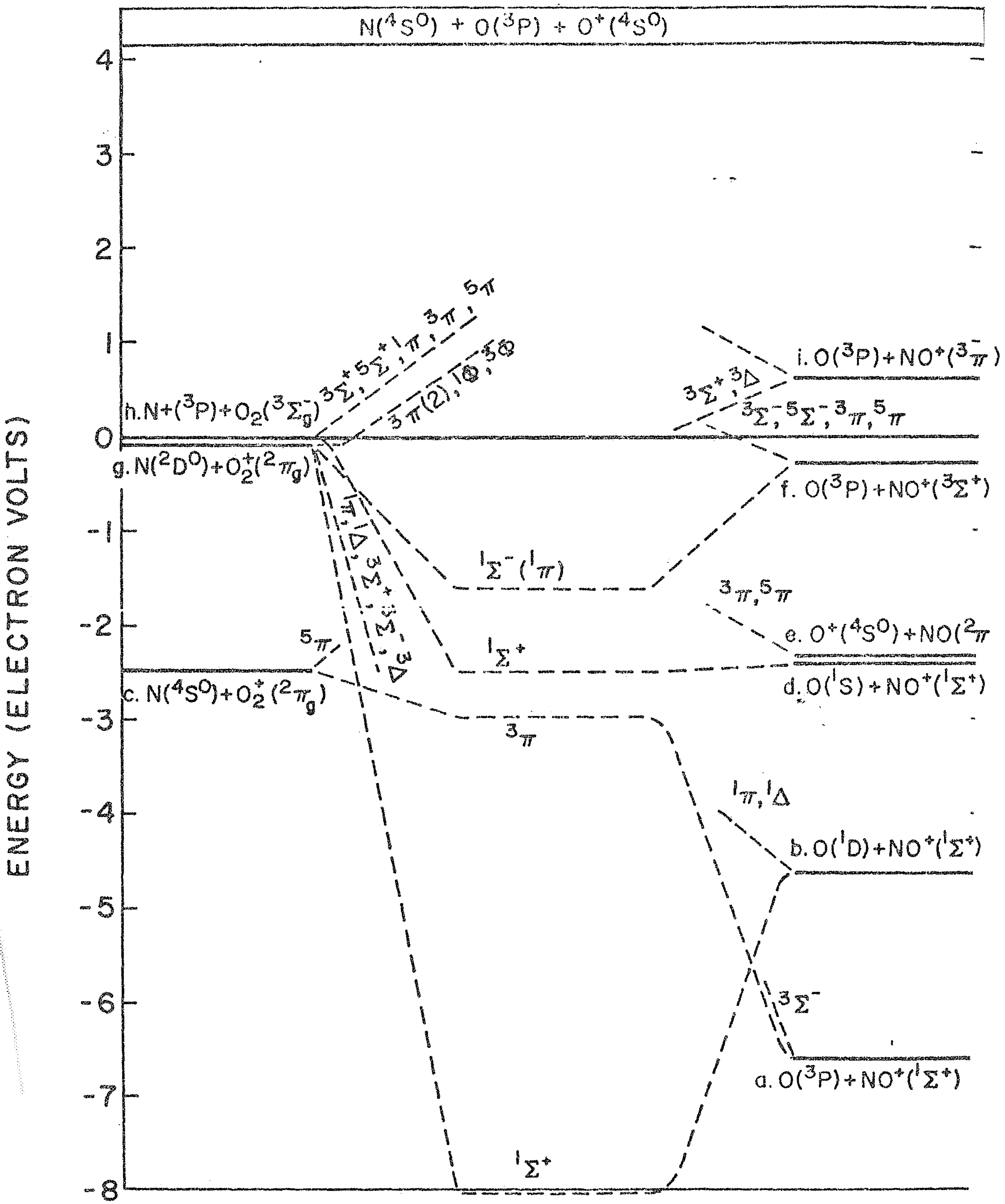


Fig 3

FIG 4



N(⁴S⁰) + O(³P) + O⁺(⁴S⁰)
ENERGY (ELECTRON VOLTS)
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
h. N⁺(³P) + O₂(³Σg⁻)
g. N(²D⁰) + O₂⁺(²πg)
c. N(⁴S⁰) + O₂⁺(²πg)
³Σ⁺, ⁵Σ⁺, ¹π, ³π, ⁵π
³π(2), ¹Δ, ³Δ
¹π, ¹Δ, ³Σ⁺, ³Σ⁻, ³Δ
⁵π
¹Σ⁻(¹π)
¹Σ⁺
³π
¹Σ⁺
i. O(³P) + NO⁺(³π)
³Σ⁺, ³Δ
³Σ⁻, ⁵Σ⁻, ³π, ⁵π
f. O(³P) + NO⁺(³Σ⁺)
³π, ⁵π
e. O⁺(⁴S⁰) + NO(²π
d. O(¹S) + NO⁺(¹Σ⁺)
¹π, ¹Δ
b. O(¹D) + NO⁺(¹Σ⁺)
³Σ⁻
a. O(³P) + NO⁺(¹Σ⁺)