$0.8,$[1] from which one infers $k_2/k_{-1} \simeq 0.4$. Thus $\gamma(0) \simeq 0.04 k_1$, which means that at zero field about one collision in 25 leads to annihilation.

The high-field anisotropy measurements represent a kind of zero-frequency magnetic resonance spectroscopy by virtue of the occurrence of the pair level-crossing resonances. The positions of these resonances can yield information concerning the zero-field splitting parameters and the orientation of the dipolar tensor while the line shapes depend on the nature and strength of the intertriplet interaction. In addition to the high-field-pair level crossings, the theory also leads one to expect single-particle level-crossing resonances when the field is oriented along a principal axis of the dipolar tensor and the strength is such that the Zeeman and zero-field splittings are about equal. Such resonances have indeed been found at the expected positions in low-field anisotropy measurements in anthracene.[4]

The theory presented here can not be regarded as confirmed until detailed calculations of field dependence and line shapes have been carried out and compared with experiment. Such calculations are currently underway. However, even at this stage it is clear that magnetic-field experiments provide a powerful tool for elucidating the details of the triplet–triplet annihilation process and for studying the spin states of triplet excitons.

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Energy Dependence of Energy Partition in Products of Direct Reactions: Crossed-Beam Studies and a New Model

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In a recent Communication,[1] we described first experiments with a crossed-beam apparatus (EVA) operating in the "hot" energy range 0.1–25 eV. It was found that a simple ion–molecule reaction, $N_2^+ + D_2 \rightarrow N_2D^+ + D$, did not involve an intermediate long-lived complex. A new model of direct reaction taking into account long-range polarization forces was described and found to provide a good representation of results obtained.[1,2]

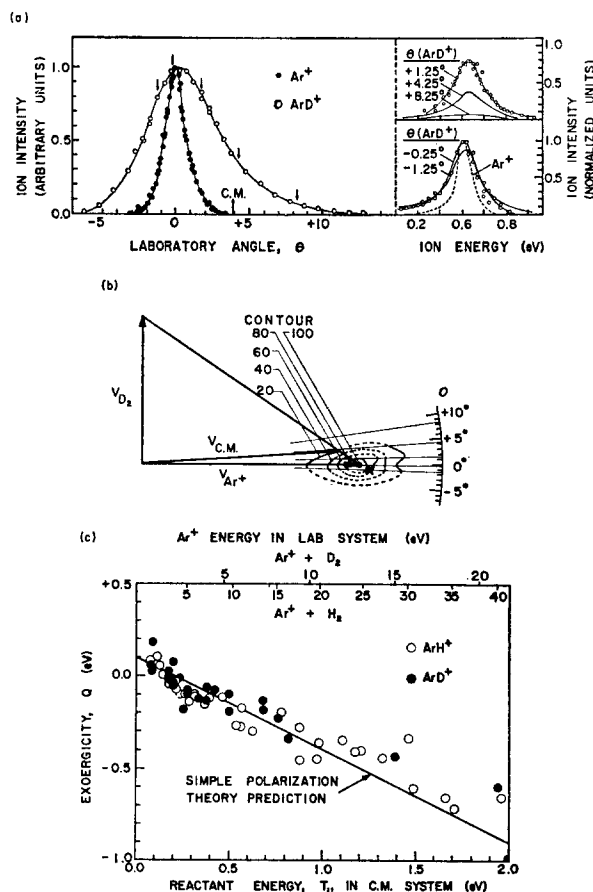We now report findings on the distribution of the reaction energy between internal and translational

FIG. 1. (a) Angular distribution (left) and energy spectra (right) taken at angles indicated by arrows for ArD^+ produced by crossing of 0.61 eV Ar^+ with thermal (55°C) D_2 molecular beam. (b) Newton diagram[2] of above data. Intensity contours are given in LAB system. $\times$ indicates position of maximum intensity after transformation to center-of-mass system (see Ref. 2). (c) Dependence of translational exoergicity Q upon reactant collision energy T_1. Plot is for maximum intensity in LAB system. (If position of maximum intensity in c.m. system were plotted, a somewhat higher intercept Q_0 would result.)

modes of the products, and on the dependence of this on initial kinetic energy. Results on the systems $Ar^+ + D_2 \rightarrow ArD^+ + D$, and $Ar^+ + H_2 \rightarrow ArH^+ + H$ are presented here.[3] They provide a test for the new model of direct reaction.

The experimental technique, involving crossed beams of monoenergetic Ar^+ and thermal hydrogen, has been described.[1,2] Typical results on the angular distribution and energy spectrum of ArD^+ at 0.61 eV LAB (0.08 eV c.m.) are shown in Fig. 1. They are summarized as intensity contours[4] on the appropriate Newton diagram. As in the case of N_2^+ reaction with D_2,[1] the data are inconsistent with a symmetrical distribution around the center of mass, which is required if an intermediate complex having a lifetime of more than a few rotational periods is formed. Furthermore, the spectator stripping model is also inadequate.[1]

From the data, the translational exoergicity of the reaction may be computed. This quantity is defined as the net conversion of internal to translational energy: $Q = T_4 - T_1$, where T_4 is the kinetic energy of the products and T_1 that of the reactants (both in the center-of-mass system). T_1 is known from the initial conditions and T_4 is computed from the measured velocity of $ArD^+(ArH^+)$ at the peak in the angular and velocity distributions. Values of Q thus determined for the position of maximum intensity[4] are shown in Fig. 1. The remarkable conclusion emerges that the translational exoergicity is not only highly energy dependent, but changes sign: at low reactant velocities there is a net conversion of internal to translational energy of products, while at higher velocities an increasing portion of the kinetic energy of the reactants appears as internal energy of products.

According to the simple polarization theory postulated earlier, the approaching reactants are accelerated towards each other by the ion–induced-dipole force between them. After atom transfer occurs, the products are similarly decelerated. Using this model, it can readily be shown[2] that for a relatively heavy ion reacting with homonuclear hydrogen the translational exoergicity is $Q \cong \frac{1}{2} P - P' - \frac{1}{2} T_1$. P and P' are ion–induced-dipole energies of the reactant and product pairs, respectively (having the form $\alpha e^2/2r_c^4$, where α is the appropriate polarizability and r_c the distance of closest approach). The single[5] adjustable parameter r_c is fitted for the lowest energy. It corresponds to a closest Ar^+–D distance of about 1.44 ± 0.15 Å.[6] (This agrees reasonably well with the known bond distance of 1.27 Å for the isoelectronic molecule DCl.)

Predictions of this model as to Q at all energies are shown as the solid line in Fig. 1. The agreement of theory and experiment for both isotopic systems supports the proposed mechanism and indicates that long-range forces dominate the dynamics of these direct reactions.

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[4] Intensities on the Newton diagram are given relative to the laboratory system. Values of Q given here correspond to the position of maximum intensity in the laboratory system (see Ref. 2, Footnotes 14, 16, and 21).

[5] There are actually two such parameters r_c, corresponding to the closest approach of the reactants, Ar^+–H_2, and closest approach of products ArH^+–H. However, they are related by half the H–H bond distance.

[6] The uncertainty quoted is based on our estimated uncertainty in the intercept of Q at 0 eV. A transformation of the Newton diagram to the c.m. is difficult,[4] but would result in a larger $Q(0 \text{ eV})$ and an Ar–D^+ distance which would be smaller by ~0.3 Å (see Ref. 2, Footnote 21).

Mercury 2537-Å Emission as a Test for $N_2(A\ ^3\Sigma_u^+)$ in Active Nitrogen*

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The main chemically reactive component of active nitrogen is ground-state N atoms.[1] Nevertheless, metastable N_2 molecules,[2] highly vibrationally excited ground-state N_2,[3] and electronically excited nitrogen atoms[4,2a] have also been directly observed or invoked to explain some reactions of active nitrogen. Dugan[5] has offered striking evidence for a metastable species in active nitrogen, apparently $N_2(A\ ^3\Sigma_u^+)$, whose concentration was first order in [N]. Recently Thrush[6a] reinterpreted the Vegard–Kaplan (A–X) emission data obtained by Noxon[6b] showing that the emission intensity was first order in [N] and in [N_2]. We will present data which, combined with these results, show that $Hg(^3P_1 \rightarrow {}^1S_0)$ emission at 2537 Å can be used to measure relative $[N_2(A\ ^3\Sigma_u^+)]$ in active nitrogen. The excitation of Hg 2537-Å emission by $N_2(A)$ was first demonstrated by Brennen and Kistiakowsky[7] and has since been employed in more complicated systems[8] as supporting evidence for the presence of $N_2(A\ ^3\Sigma_u^+)$. However, the data shown here are the first direct kinetic analysis of the excitation processes.

Nitrogen atoms were generated by a microwave discharge through pure N_2 or N_2/Ar mixtures in an ordinary discharge flow apparatus. Values of [N] were determined by NO titration. Mercury vapor was added to the flow stream with a metered flow of nitrogen or argon which had been saturated with mercury at room temperature. Figure 1 shows that the intensity (I) is first order in [N], and it was also shown to be first order in [Hg] and total pressure, with N_2 or Ar carrier gas. I was independent of both time after the discharge and contact time with the Hg. This shows that the exciting species is being continuously generated in active N_2.

The simplest explanation of the observations is the