

**Product rotational alignment in the excitation transfer reaction  $\text{Ar}(3\text{P } 2)+\text{N}_2\text{Ar}+\text{N}_2(\text{C } 3\text{u})$**

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# Product rotational alignment in the excitation transfer reaction



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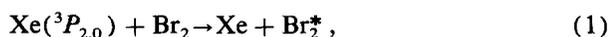
The velocity dependence of the  $\text{N}_2(C)$  rotational alignment from the title excitation transfer reaction was studied over the collision energy range 42–460 meV, using a beam-gas time-of-flight method. The alignment was found to be positive, and to increase approximately linearly with energy: the extrapolated line has a large positive intercept, suggesting that the alignment persists down to zero energy. The present results, together with previous studies of this reaction, are consistent with a model in which the reaction occurs preferentially in the plane of rotation of the  $\text{N}_2$ . It is suggested that this steric effect is due primarily to the orbital overlap requirements of the electron exchange mechanism. The polarization of the fluorescence from the dissociative excitation reactions of  $\text{Ar}^* + \text{CS}_2$ ,  $\text{Ar}^* + \text{H}_2\text{O}$ ,  $\text{Kr}^* + \text{CS}_2$ , and  $\text{Xe}^* + \text{BrCN}$  was also measured and found to be zero at all velocities.

## I. INTRODUCTION

The first studies of reaction product rotational alignment were performed by Herschbach and co-workers using the electric deflection technique,<sup>1–4</sup> and the first study of product rotational alignment using fluorescence polarization was done by Jonah, Zare, and Ottinger.<sup>5</sup> Since then a number of studies of fluorescence polarization have been carried out to obtain the product rotational alignment.<sup>6–19</sup> Most product alignment studies have been on atom transfer reactions of the type  $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ , occurring on highly attractive potential surfaces, i.e., reactions of alkali metal,<sup>1–4</sup> alkaline earth metal,<sup>5–7</sup> and metastable rare gas atoms<sup>8–19</sup> with halide molecules. It is found that in these cases there is strong coupling between the reactant relative velocity vector  $\bar{k}$  and the product angular momentum  $\bar{J}$ , which leads to strong product alignment effects.

In excitation transfer processes of the type  $\text{A}^* + \text{BC} \rightarrow \text{A} + \text{BC}^*$  which involve potential surface crossings but no mass transfer, this coupling might be expected to be weaker. However, two general types of effects may lead to alignment of the molecular product: the effect of anisotropic potential energy surfaces on inelastic scattering dynamics,<sup>20</sup> and effects resulting from the steric dependence of the electronic transition between the incoming and outgoing potential surfaces. Considerable theoretical work has been done on product alignment in rotationally inelastic collisions,<sup>20,21</sup> which shows that such alignment can be expected if there is significant anisotropy in the long range potential.

Hennessy and Simons<sup>10</sup> have studied the product alignment from the excitation transfer reaction (1), and found positive  $\text{Br}_2^*$  alignment



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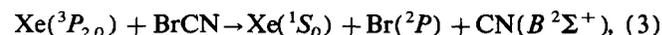
which decreased with increasing reactant velocity, in contrast to the positive velocity dependence found with the atom transfer reactions. They explained this in terms of scattering from an attractive anisotropic potential at low velocities, which becomes more repulsive with increasing velocity.

In the present work we have studied the product alignment from reaction (2):



This reaction has become a prototype electronic excitation transfer process, by virtue of its inherent properties and the extensive study devoted to it, using both flowing afterglow<sup>22–33</sup> and molecular beam<sup>18,34–43</sup> techniques. Although the beam contained both  $\text{Ar}(^3P_2)$  and  $\text{Ar}(^3P_0)$ , the results of this work can be considered to be essentially for  $^3P_2$ , since the  $^3P_2/^3P_0$  ratio is expected to be about the statistical value of 5, and the  $^3P_2$  cross section has been found to be more than twice that for  $^3P_0$ .<sup>25,30</sup> The  $^3P_2$  state is 521 meV above the ( $v' = 0, J' = 1$ ) level of the  $\text{N}_2(C)$  state, and the  $^3P_0$  state is 174 meV above the  $^3P_2$ .  $\text{Ar}^* + \text{N}_2$  quenching is found to produce only  $\text{N}_2(C^3\Pi_u)$ ,<sup>33</sup> which radiates to  $\text{N}_2(B^3\Pi_g)$ , and this in turn radiates to the metastable  $\text{N}_2(A^3\Sigma_u)$  state. The  $C \rightarrow B$  emission in the ultraviolet is easily separated from the  $B \rightarrow A$  emission in the visible, using broadband light filters. We find that the  $\text{N}_2(C)$  has a positive alignment, which increases linearly with average collision velocity over the range 700–2330 m/s (collision energy range is 42–460 meV).<sup>44</sup>

Dissociative excitation of triatomic molecules (i.e., reactions of the type  $\text{A}^* + \text{BCD} \rightarrow \text{A} + \text{B} + \text{CD}^*$ ) is another kind of nonadiabatic process which occurs in metastable rare gas atom collisions. The diatomic product alignment from only one such reaction has been studied previously. Hennessy, Ono, and Simons<sup>11</sup> studied reaction (3):



and found no alignment of the  $\text{CN}^*$  over the collision energy range 70–750 meV. In the present work we have studied this reaction with improved signal/noise over the range 42–225 meV, for comparison with the results on reaction (2), and we also find no alignment.

A basic requirement for obtaining the alignment from the polarization without spectral resolution of the rotational lines is that the diatomic product fluorescence be from parallel-type electronic transitions, i.e., ones for which the transition dipole moment  $\bar{\mu}$  is along the bond. For perpendicular-type transitions, measurement of the polarization of the resolved  $P$ -,  $Q$ -, or  $R$ -branch lines is required (see Appendix).<sup>5,6,45</sup> The degree of rotational alignment in the center-of-mass (c.m.) coordinate system was determined as follows. Let the beam axis (the axis of symmetry in beam-gas experiments) be  $z$  and the unit vector along this axis be  $\hat{z}$ . The unit vectors corresponding to the relative velocity vector  $\bar{k}$  and the product rotational angular momentum vector  $\bar{J}'$  are  $\hat{k}$  and  $\hat{J}'$ , respectively. As a result of the cylindrical symmetry of  $\hat{k}$  and  $\hat{J}'$  about  $\hat{z}$ , it can be shown that<sup>5,6,14,46</sup>

$$\langle P_2(\hat{J}' \cdot \hat{z}) \rangle = \langle P_2(\hat{J}' \cdot \hat{k}) \rangle \langle P_2(\hat{k} \cdot \hat{z}) \rangle, \quad (4)$$

where  $P_2$  is the second Legendre moment, e.g.,

$$P_2(\hat{J}' \cdot \hat{k}) = \frac{1}{2}[3(\hat{J}' \cdot \hat{k})^2 - 1] = \frac{1}{2}(3 \cos^2 \theta - 1), \quad (5)$$

and  $\theta$  is the angle between  $\hat{J}'$  and  $\hat{k}$ .

As described in the Appendix, it is convenient to define the degree of alignment as

$$A = -2 \langle P_2(\hat{J}' \cdot \hat{k}) \rangle. \quad (6)$$

It is then advantageous to use the same functional form to define the degree of polarization in terms of  $(\hat{J}' \cdot \hat{z})$ . Therefore, for parallel-type transitions we define the polarization quotient  $Q$  as

$$Q = -2 \langle P_2(\hat{J}' \cdot \hat{z}) \rangle. \quad (7)$$

It can be shown that<sup>14</sup>

$$Q = 4 \left[ \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \right]. \quad (8)$$

The polarization quantity inside the brackets has been designated  $R$  by Simons and co-workers.<sup>14</sup>  $R$  is measured in the experiment, giving  $\langle P_2(\hat{J}' \cdot \hat{z}) \rangle$ . For a thermal gas and a beam with a known velocity distribution, the kinematic blurring term  $\langle P_2(\hat{k} \cdot \hat{z}) \rangle$  in Eq. (4) can be determined by a Monte Carlo calculation.<sup>6,14,19</sup>  $\langle P_2(\hat{J}' \cdot \hat{k}) \rangle$  is then obtained from Eq. (4) and from Eq. (5) one can obtain  $\langle \cos^2 \theta \rangle$ , which is the basic dynamical quantity of interest.

It is to be expected that the dissociative excitation of triatomic molecules producing diatomics with perpendicular-type transitions would give negligible polarization of the total fluorescence, since the additional degrees of freedom will tend to reduce the product alignment, and the polarization will be zero regardless of the alignment if the intensities of the  $P$ ,  $Q$ , and  $R$  branches are equal. Since the fluorescence in other ways duplicates that seen from parallel-type transitions (e.g., in the spatial distribution), reactions giving zero polarization may serve as reference sources for measuring any zero offset in the  $Q = 0$  base line. To test this idea, we measured  $Q$  as a function of velocity for three reactions of

this type. They gave identical results, and established that there was a small zero offset in the experimental base line.

## II. EXPERIMENTAL

The beam-gas time-of-flight (TOF) method used in these studies has been described in detail previously.<sup>19</sup> The metastable atoms were formed by passing an effusive noble gas atom beam through a cold cathode discharge. The metastable beam was pulsed by a rotating wheel and after a 30 cm flight path the beam passed through the target gas cell. The fluorescence from the target molecules was viewed at right angles to the metastable beam by two identical optical detection systems, which consisted of light filters to isolate the radiation of interest, thin film linear polarizers, and photomultiplier (PM) tubes. The two polarizers were set so that one passed light polarized along the metastable beam and the other passed light polarized perpendicular to the beam. By simultaneously monitoring the light intensities observed by the two photomultiplier tubes as a function of the metastable flight time, the degree of product molecule fluorescence polarization with respect to the beam direction was determined as a function of the metastable velocity.

For the  $\text{Ar}^*/\text{N}_2$  experiments the gas cell was cooled to 150 K, whereas for the  $\text{Xe}^*/\text{BrCN}$  experiments the cell was heated to 320 K to prevent condensation of the gas on the cell windows. In order to cover a wider velocity range, the  $\text{Ar}^*/\text{N}_2$  experiments were carried out with source temperatures of 273 and 500 K, whereas in the  $\text{Xe}^*/\text{BrCN}$  experiments the Xe source was operated at room temperature. In the  $\text{Ar}^*/\text{CS}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{Kr}^*/\text{CS}_2$  experiments both the beam source and gas cell were operated at room temperature.

The reproducibility of the polarization measurements was determined by the relative sensitivities of the two PM tubes and the signal-to-noise ratio (S/N). The  $Q = 0$  base line was determined by rotating one of the polarizers so that it was parallel with the other one and measuring the ratio of the PM signals. This calibration was carried out every 20–30 min during the experiments, which lasted several hours, to correct for drifts in the relative sensitivity of the two detection systems. It was found that drifts in the sensitivities could change  $Q$  by as much as  $\pm 0.02$ . Since the drift was usually smaller than this, and tended to average out in repetitive runs, the average drift error was much less; as discussed in the next section, the data from the four dissociative excitation reactions indicates that it was only about  $\pm 0.002$ .

## III. RESULTS AND DISCUSSION

### A. Fluorescence polarization measurements on dissociative excitation reactions

The results from the dissociative excitation experiments are shown in Table I. The fluorescence from the first three reactions is from perpendicular-type transitions ( $\Delta\Lambda = 1$ ), and so the polarization was expected to be small or negligible. In all three cases the measured  $Q$  was independent of velocity. The average value  $\bar{Q}$  and root-mean-square (rms) error for each case is given in the table, and for the three taken together  $\bar{Q} = -0.011 \pm 0.001$ , with an average rms

TABLE I. Polarization measurements for diatomic fluorescence from triatomic dissociative excitation.

Reaction	Collision energy range (meV) <sup>a</sup>	Experimental polarization quotient $Q^b$
$\text{Ar}^* + \text{CS}_2 \rightarrow \text{Ar} + \text{S} + \text{CS}(A^1\Pi)$ $\text{CS}(A^1\Pi) \rightarrow \text{CS}(X^1\Sigma) + h\nu$	32–193	$-0.011 \pm 0.014$
$\text{Kr}^* + \text{CS}_2 \rightarrow \text{Kr} + \text{S} + \text{CS}(A^1\Pi)$ $\text{CS}(A^1\Pi) \rightarrow \text{CS}(X^1\Sigma) + h\nu$	50–92	$-0.010 \pm 0.002$
$\text{Ar}^* + \text{H}_2\text{O} \rightarrow \text{Ar} + \text{H} + \text{OH}(A^2\Sigma^+)$ $\text{OH}(A^2\Sigma^+) \rightarrow \text{OH}(X^2\Pi) + h\nu$	32–90	$-0.012 \pm 0.003$
$\text{Xe}^* + \text{BrCN} \rightarrow \text{Xe} + \text{Br} + \text{CN}(B^2\Sigma^+)$ $\text{CN}(B^2\Sigma^+) \rightarrow \text{CN}(X^2\Sigma^+) + h\nu$	42–225	$-0.014 \pm 0.005$

<sup>a</sup> The polarization was determined as a function of velocity using the TOF method described in the text.

<sup>b</sup> Averages determined from 8–10 values measured over the energy range are given. Error limits are the rms errors. As discussed in the text, the true  $Q$  values are zero, and the experimental values are due to a small negative zero offset.

error of  $\pm 0.006$ . The only reasonable explanation for this identical behavior is that we had a determinate error in our measurements of  $-0.011$ . This could have been caused by various effects. For example, unpolarized fluorescence could have acquired a small amount of polarization from passing through the cell windows, light filters, and phototube windows, or from reflection from the cell walls.

The absolute accuracy of the polarization measurements was not determined. Measurement of the accuracy is not a simple matter, since a way must be found to calibrate the entire optical system using a light source which duplicates the characteristics of the fluorescence. Reaction reference standards are one solution to the problem, e.g., the reactions  $\text{Xe}^* + \text{HX} \rightarrow \text{XeX}^* + \text{H}$ , where X is Cl, Br, or I. These reactions are highly constrained kinematically, and the polarization from the  $\text{XeX}^*$  excimers has been found by Simons and co-workers<sup>15</sup> to reach the kinematic limit (see Appendix) at high velocities. Our data<sup>19</sup> on  $\text{Xe}^*/\text{HBr}$  agree with theirs at our highest energy point: our alignment was 7% less than theirs, but within their error bars. Their three lower points are below ours. Thus there is disagreement about the shape of the curve, but qualitative agreement about the approach to the kinematic limit, and the comparison indicates that our alignment is not systematically lower than theirs. In the case of  $\text{Xe}^*/\text{HCl}$ , our highest point was 28% below theirs. This is an endoergic reaction for  $\text{Xe}(^3P_2)$  and we observed it below the threshold for this state, indicating that the  $^3P_0$  state reaction was also important in our case. Further resolution of this discrepancy will require additional study.

For the  $\text{Xe}^*/\text{BrCN}$  reaction which gives fluorescence from a parallel-type transition ( $\Delta\Lambda = 0$ ) we obtained  $Q = -0.014 \pm 0.005$ , in agreement with the results from the perpendicular-type transitions. This confirms the finding of Hennessy *et al.*<sup>11</sup> that there is no significant alignment of the  $\text{CN}(B)$  from this reaction. As they have discussed, this result together with other information on the reaction indicates that it occurs via formation of an ionic complex  $(\text{Xe}^+\text{BrCN}^-)^*$ , which dissociates to  $\text{XeCN}^*$ , followed by predissociation to  $\text{Xe} + \text{CN}(B)$ . Obviously there is ample

opportunity for angular momentum scrambling in such a mechanism, especially if the complexes involved are “loose,” allowing dissociation from bent configurations.

In previous work on the steric dependence of the  $\text{Ar}^* + \text{CS}_2$  reaction,<sup>47</sup> we carried out an auxiliary experiment to measure the product polarization, to show that the fluorescence emission intensity is essentially isotropic. In that work we obtained  $Q = -0.031 \pm 0.007$ , which proved the point, but is also three times the zero offset found in the present work. This appears to be an anomalous result, in view of the excellent agreement found between the four triatomic reactions in the present work.

In our previous polarization paper<sup>19</sup> we observed negative polarization from the  $\text{Xe}^*/\text{Cl}_2$ ,  $\text{Br}_2$  systems at low velocities. The lowest data points were  $Q = -0.014$  for  $\text{Xe}^*/\text{Cl}_2$  and  $Q = -0.053$  for  $\text{Xe}^*/\text{Br}_2$ . The  $\text{Xe}^*/\text{Cl}_2$  value is only slightly larger than the zero offset found in the present work (and half that found in the previous  $\text{Ar}^*/\text{CS}_2$  work), so this point by itself is not significant. The  $\text{Xe}^*/\text{Br}_2$  negative polarization is well outside even the previous  $\text{Ar}^*/\text{CS}_2$  zero offset, and therefore is significant. Equally important, the trend of the data indicates in both cases that  $Q$  becomes negative before approaching zero at low velocities due to the  $X_2$  isotropy.

## B. $\text{Ar}(^3P_2) + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2(C^3\Pi_u)$

### 1. $\text{N}_2(C)$ alignment

The polarization  $Q$  and alignment  $A$  are shown as functions of velocity in Fig. 1. We have added 0.011 to the experimental  $Q$  data points, to correct for the zero offset discussed in the previous section. We find that  $A$  increases slowly and nearly linearly with energy over the range 42–463 meV. From Eqs. (5) and (6) we have that  $\langle \cos^2 \theta \rangle = (1 - A)/3$ . Over the experimental energy range  $A$  increases from 0.174 to 0.242 (based on the least-squares fit to the  $A$  vs velocity data), giving  $\langle \cos^2 \theta \rangle$  from 0.275 to 0.253. If we call the angle corresponding to  $\langle \cos^2 \theta \rangle$  the characteristic angle  $\theta_c$  (i.e., the angle corresponding to the root-mean-square  $\cos \theta$ ), then  $\theta_c$  ranges from  $58.3^\circ$  to  $59.8^\circ$ . These values are

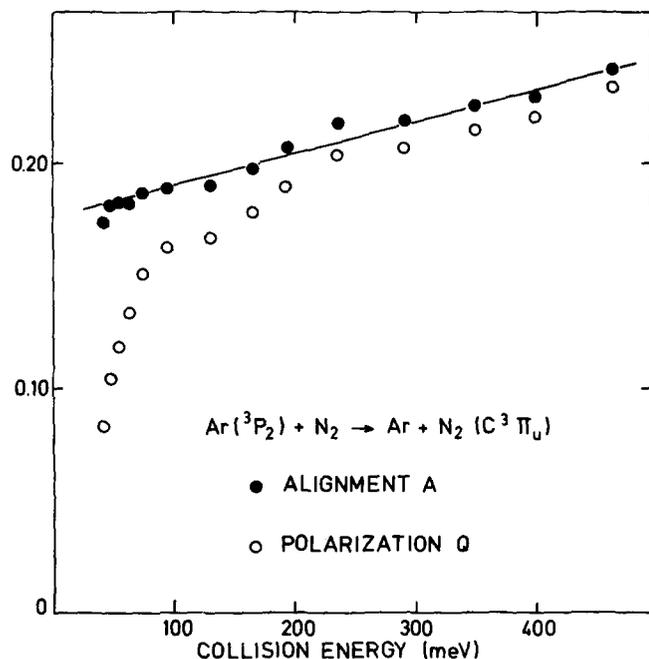


FIG. 1. Fluorescence polarization and alignment of  $\text{N}_2(C)$  from the excitation transfer reaction of  $\text{Ar}(^3P_2)$  with  $\text{N}_2$ .

$3.6^\circ \pm 0.2^\circ$  and  $5.1^\circ \pm 0.2^\circ$  above the isotropic value  $54.7^\circ$ , where the error limits are based on the data in Table I and the discussion in Sec. III A.

In the product alignment study<sup>10</sup> of  $\text{Xe}^* + \text{Br}_2 \rightarrow \text{Xe} + \text{Br}_2^*$  it was found that the alignment decreased at high energies, but in the energy range of the present work it was constant within experimental error, with a value of 0.19. Thus the results for these two excitation transfer reactions are similar in this range: the alignments are both quite insensitive to collision energy, and the average alignments are nearly the same. This similarity is surprising, in view of the fact that reaction (1) occurs via a highly attractive long-range potential, and is a minor channel in competition with  $\text{XeBr}^*$  formation.

It is interesting to compare the  $\text{Ar}^*/\text{N}_2$  alignment data in Fig. 1 with those from our previous study of the  $\text{Xe}^*/\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$  systems.<sup>19</sup> (In making these comparisons we have multiplied our previous  $A$  function by 3—see the Appendix.) The  $A$  vs velocity behavior is very different: the  $\text{Xe}^*/\text{X}_2$  plots are nonlinear, have much steeper slopes (except for  $\text{I}_2$  above about 100 meV), and drop below that of  $\text{Ar}^*/\text{N}_2$  below 80–100 meV. For  $\text{Xe}^*/\text{I}_2$   $A$  is about the same as that from  $\text{Ar}^*/\text{N}_2$  in the 100–400 meV region. For  $\text{Cl}_2$  and  $\text{Br}_2$  the  $A$  curves continue to rise steeply above that of  $\text{Ar}^*/\text{N}_2$  above the crossing points at about 80–90 meV, and fall off rapidly at lower energies, appearing to become negative below about 40 meV. The important point for this discussion is that the  $\text{N}_2(C)$  alignment is approximately as strong, or stronger, than that from  $\text{Xe}^*/\text{I}_2$  over the 40–400 meV range and is also stronger than that from  $\text{Xe}^*/\text{Cl}_2$ ,  $\text{Br}_2$  below about 80 meV. Some questions about the quantitative aspects of the above comparisons have been raised by recent work of Johnson *et al.*<sup>16</sup> on the  $\text{Xe}^*/\text{X}_2$  systems, but this is not expected to change the general picture given above.

## 2. Summary of previous work

In this section we summarize the highlights of previous work relevant to the present discussion. This summary is not comprehensive and references to other work on this system can be obtained from the references given. After completing this paper we received a preprint of reference 49 by Beijerinck and co-workers: this paper is an extensive study of reaction (2) and includes new results on the energy dependence of the product rotational and vibrational distributions.

The question of whether  $\text{Ar}^* + \text{N}_2$  produces  $\text{N}_2(B)$  directly in competition with  $\text{N}_2(C)$ , or only by radiative cascade from  $\text{N}_2(C)$ , has been a subject of controversy,<sup>24,29,43</sup> but that has now been resolved in favor of the latter conclusion.<sup>33,48</sup> For the reasons given in Sec. I, both the beam and flowing afterglow results can be interpreted essentially in terms of the  $^3P_2$  state.

(a) *Reaction cross section:* The reaction cross section has been studied by several groups in crossed molecular beams.<sup>34–36,38,43</sup> Parr and Martin<sup>36</sup> determined the relative cross section over the 20–800 meV range using a mechanically pulsed  $\text{Ar}^*$  beam and time-of-flight (TOF) velocity dispersion. They obtained a cross section which increases linearly with collision energy up to about 70 meV and extrapolates to zero at zero energy. Winicur and Fraites<sup>34</sup> derived a threshold energy of 8 meV from the analysis of  $\text{Ar}^*$  differential scattering data. From these results we believe the threshold energy to be 0–10 meV.

Parr and Martin found that the cross section rises to a maximum at about 250 meV and decreases at higher energies. Recently Tabayashi and Shobatake<sup>44</sup> have measured the relative cross section from 0.4–2.5 eV using an arc-heated beam and TOF velocity dispersion. They observe a decreasing cross section that agrees well with that of Parr and Martin in the overlapping energy range of 0.4–0.8 eV. Parr and Martin normalized their relative cross section to the room temperature rate constant of Kolts *et al.*<sup>27</sup> of  $2.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  to obtain the absolute cross section and Tabayashi and Shobatake normalized their cross section to that of Parr and Martin. However, Sadegi and Setser<sup>33</sup> have reported a revised rate constant of  $3.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and therefore both these cross sections should be multiplied by 1.8. This correction should also be applied to the recent cross section measurements of Beijerinck and co-workers.<sup>49</sup> The revised cross section has a maximum value of  $14 \text{ \AA}^2$  at 250 meV. At 50 meV it is about half the value derived by Winicur and Fraites at this average energy from elastic scattering data. At this energy they found the excitation transfer scattering to be primarily backward ( $> 90^\circ$ ) in the center-of-mass system, although it extended to angles as small as  $40^\circ$ .

(b) *Vibrational distributions:* The vibrational distribution of  $\text{N}_2(C)$  has been studied in the present collision energy range in crossed beam<sup>39,43</sup> and beam-gas<sup>42</sup> experiments. Krenos and Bel Bruno<sup>42</sup> obtained  $v' 2/1/0$  ratios of 0.04/0.26/1 at 48 meV and 0.06/0.29/1 at 160 meV. Cutshall and Muschlitz<sup>39</sup> found an oscillatory behavior in the  $v' 1/0$  ratio over the collision energy range 50–400 meV, with the ratio varying between 0.26 and 0.30. Tabayashi and Shobatake<sup>43</sup> found  $2/1/0$  ratios of 0.08/0.28/1 with error bars of  $\pm 0.02$  over the 0.4–2.5 eV range, which agrees with the  $1/0$  ratio of

Beijerinck and co-workers<sup>49</sup> over the same range. Thus there is good agreement between all of the vibrational distribution data obtained from molecular beam experiments; the branching ratio into  $v' = 2$  perhaps doubles from 50 to 400 meV, but there is only a 15% variation in the  $v' = 1$  branching ratio. Stedman and Setser<sup>23</sup> also studied the vibrational populations in a flowing afterglow, and obtained 2/1/0 ratios of approximately 0.05/0.20/1 at room temperature (average collision energy, 40 meV).

Cutshall and Muschlitz explained the oscillating 1/0 ratio in terms of a simple Lipeles model,<sup>50</sup> i.e., a stretching of the perturbed  $\text{N}_2(X)$  bond at low collision energies and a compression of the bond at high collision energies gave a fit to the observed changes. Gislason *et al.*<sup>51</sup> used a more elaborate model to explain the results. They also assumed a shift in the  $\text{N}_2(X)$  bond length when  $\text{Ar}^*$  is about 3 Å from  $\text{N}_2$ , due to the approach of the  $\text{Ar}^+ + \text{N}_2^-$  curve to the  $\text{Ar}^* + \text{N}_2$  neutral curve at this point. However, they followed the time evolution of the vibrational wave function throughout the collision, using time-dependent quantum mechanics. With this approach they were able to fit both the  $v' = 1/0$  oscillations and the average 2/1/0 branching ratio.

There is a hint of an oscillation in the  $A$  vs  $E$  plot in Fig. 1, which corresponds to the oscillation in the  $v' = 1/0$  ratio; the minimum corresponds roughly to the 1/0 maximum and the maximum to the 1/0 minimum. This is the correlation that one would expect; the rotational excitation should go inversely to the vibrational excitation and  $A$  should decrease with decreasing rotational excitation. This suggests that the small oscillation in  $A$  is real, but further work will be needed to confirm this.

The vibrational branching ratios are far removed from the unperturbed  $\text{N}_2(C-X)$  Franck-Condon factors. Krenos and Bel Bruno<sup>42</sup> found that the 1/0 ratio as a function of collision energy is well represented by the Franck-Condon factors multiplied by the density of exit channel states. However, Sadeghi and Setser<sup>33</sup> and Nguyen and Sadeghi<sup>30</sup> conclude that this agreement is fortuitous, because the model does not work for the excitation transfer reactions of  $\text{Ar}(^3P_0)$ ,  $\text{Kr}(^3P_2)$ , and  $\text{Xe}(^3P_2)$  with  $\text{N}_2$ .

(c) *Rotational distributions:* The  $\text{N}_2(C)$  rotational distributions have been studied by Muschlitz and co-workers<sup>39,40</sup> in crossed supersonic beams. Lishawa *et al.*<sup>40</sup> derived the rotational distributions for  $v' = 0$  and  $v' = 1$  from the rotationally unresolved band spectra, using a spectral simulation program. The  $v' = 0$  band was measured at collision energies of 76, 89, and 161 meV; Boltzman distributions were found to fit the band shapes, giving rotational temperatures of 1700, 1600, and 2200 K at the respective energies. The  $v' = 1$  distribution was studied only at 161 meV; it could be fit by a Boltzmann distribution at 4000 K with a sharp cutoff at the maximum  $J'$  allowed by energy conservation.

The beam results obtained under single collision conditions from rotationally unresolved bands may be compared with those of Setser *et al.*<sup>24</sup> and Derouard *et al.*<sup>31</sup> from resolved spectra under flowing afterglow conditions. Their results agree qualitatively with those of Lishawa *et al.*; all find  $J'$  states populated up to the energetic limit (of the order of

$J' = 50$  for  $\text{Ar}(^3P_2)$ , depending on  $v' = 0$  vs  $v' = 1$ , and the collision energy). Setser *et al.*<sup>24</sup> obtained a rotational distribution at a pressure of 1 Torr, which is similar to that of Lishawa *et al.*, and they found that different portions of their distribution could be characterized by temperatures of approximately 950 and 2300 K. Considering that there may have been significant rotational quenching at 1 Torr and the uncertainties involved in extracting distributions from unresolved spectra in the beam work, the flowing afterglow and beam results are in reasonable agreement.

Nguyen and Sadeghi<sup>30</sup> have determined the rotational and vibrational distributions of  $\text{N}_2(C)$  excited by state-selected  $\text{Ar}(^3P_2)$  and  $\text{Ar}(^3P_0)$  at lower pressures, where the rotational relaxation prior to fluorescence was negligible. They found that the bimodal rotational distribution indicated previously<sup>24</sup> at 300 K is greatly enhanced into two distinct peaks at 90 K, with both  $\text{Ar}(^3P_2)$  and  $\text{Ar}(^3P_0)$  excitation.

(d) *Fine structure states:* The  $\text{N}_2(C \rightarrow B)$  spectrum has well separated rotational lines, each consisting at high resolution of closely-spaced triplet structure, characteristic of high  $J$  of "an almost pure Hund's case (b) coupling."<sup>31</sup> For case (b) coupling the net rotational ( $N$ ) and electronic orbital angular momentum ( $\Lambda$ ) quantum number is  $K$ , and the sum of this with the electronic spin quantum number  $S$  gives the total angular momentum quantum number  $J = K, K \pm 1$ . This produces the triplet lines, which are designated by  $F_1, F_2,$  and  $F_3$ , corresponding to the  $^3\Pi_0, ^3\Pi_1,$  and  $^3\Pi_2$  states in case (a) notation. Setser *et al.*<sup>24</sup> found several unusual features in the spectrum: alternation of intensities between the even and odd  $\text{N}_2(C)$   $K'$  states; unequal intensities of the triplet lines for a given  $K'$ ; and anomalous intensity alternation between the  $\Lambda$  doublets of the  $F_1$  lines (which were the only spin state lines for which the  $\Lambda$  doublets could be resolved). The latter observation explained the alternating intensities of the  $K'$  states. Derouard *et al.*<sup>31</sup> studied the spectrum excited selectively by  $\text{Ar } ^3P_2$  vs  $^3P_0$  and found strong differences in the fine structure. Their results with  $\text{Ar}(^3P_2)$  were in good agreement with those of Setser *et al.* using unselected  $\text{Ar}^*$ , and they interpreted the unequal  $F$  line intensities (spin state populations) as evidence that spin-orbit interaction is important in the reaction complex.

The  $\Lambda$ -doublet levels favored by the reaction belong to the half-filled  $2\pi_g$  orbital lying preferentially (to varying degrees, depending on the rotational and spin sublevel state) in the plane of rotation of the molecule,<sup>24,31,52</sup> whereas the other  $\Lambda$ -doublet orbital lies perpendicular to this plane. Following Sester and co-workers,<sup>24,52</sup> we refer to these respective orbitals as  $\pi^+$  and  $\pi^-$ , since they have + and - symmetry with respect to reflection in the plane of rotation.

Alexander and Dagdigan<sup>53</sup> have discussed the orbital densities in  $\Pi$  states and their symmetries with respect to the plane of rotation (POR). They find that for  $^3\Pi_1$  states there is + or - symmetry of the orbitals for both case (a) and (b) coupling. For  $^3\Pi_{0,2}$  states the electron distributions of both  $\Lambda$ -doublet states are cylindrically symmetric with case (a) coupling and become increasingly aligned with respect to the POR as the degree of case (b) coupling increases with molecular rotation. The degree of case (b) coupling depends on the relative magnitude of the spin-orbit coupling con-

stant  $A$  vs  $BJ$ , where  $B$  is the rotational constant,<sup>54</sup> i.e.,  $BJ \ll A$  gives case (a) coupling, and  $BJ \gg A$  tends to give case (b) [and eventually case (d)] coupling. For the  $\text{N}_2(C^3\Pi_u)$  state  $A = 39.2 \text{ cm}^{-1}$  and  $B = 1.82 \text{ cm}^{-1}$ ,<sup>55</sup> giving  $BJ = A$  for  $J = 22$ , which is about the middle of the  $\text{N}_2(C)$  rotational distribution.

Sadeghi and co-workers<sup>31</sup> found a  $\pi^+$  propensity of 3 for the  $^3\Pi_0$  state in the range  $N = 35\text{--}45$ . The fact that the intensity alternation did not show any trend with  $N$  in this range indicates that there is little, if any, decrease of the  $\pi^+$  propensity by case (a) coupling and therefore the value of 3 can be taken as a true probe of the reaction dynamics, as discussed in the next section.

### 3. Reaction models

The  $\text{N}_2(C^3\Pi_u)$  valence molecular orbital configuration is  $3\sigma_g^2 4\sigma_u 5\sigma_g^2 1\pi_u^4 2\pi_g$ ; these orbitals (with the exception of the  $3\sigma_g$ ) are depicted in Fig. 2. The  $\text{N}_2(C)$  state is formed by promotion of an electron from  $4\sigma_u$  to  $2\pi_g$ . This takes place by an exchange process; the  $\text{Ar}^*$   $4s$  electron transfers to an empty  $2\pi_g$  orbital and a  $4\sigma_u$  electron transfers to the half-filled  $3p$  orbital. These two electron transfers do not necessarily have to be simultaneous, and in fact there is good reason to believe that the reaction may proceed by sequential transitions via an intermediate potential.<sup>33,51,52</sup>

Setser and co-workers<sup>24,52</sup> interpreted the preference for forming  $\pi^+$  states to mean that there is a tendency for the plane of the three nuclei (which we will call for convenience the “complex” plane) to be a plane of  $+$  symmetry throughout the collision, i.e., the half-filled  $3p$  orbital of  $\text{Ar}^*$  locks onto this plane. They argued that if the  $3p$  orbital lies in the complex plane ( $+$  symmetry), then only  $\text{N}_2(C)$  states

of  $+$  symmetry can be formed. However, this is not a sufficient condition, since the final rotational plane of  $\text{N}_2(C)$  can lie at any angle with respect to the complex plane. Consider, for simplicity, a collision in which the  $\text{Ar}^*$  approaches perpendicular to the plane of rotation of  $\text{N}_2$  with zero impact parameter and departs in the same way. Then the complex plane remains perpendicular to the  $\text{N}_2$  plane of rotation and rotates with  $\text{N}_2$ . The  $\text{Ar}^* p$  orbital can, in principle, lock onto this plane with either  $+$  or  $-$  symmetry, but it cannot have  $+$  or  $-$  symmetry with respect to the plane of rotation of the  $\text{N}_2$  because it is not centered in this plane. Thus the Setser symmetry condition must be made more restrictive; the complex plane must also coincide roughly with the plane of rotation of the  $\text{N}_2$  before and after the collision.

Even for the example above with the complex plane perpendicular to the  $\text{N}_2$  rotation plane, the  $\Lambda$ -doublet state may act as a stereochemical indicator of where the electron came from, by reflecting the orbital overlap that produced it. Thus we must distinguish between symmetry arguments vs orbital overlap (and potential surface) arguments in seeking explanations for preferred  $\pi^+$  formation. In our view, the symmetry argument of Setser and co-workers does not mean that the  $\Lambda$ -doublet symmetry controls or directs the reaction—rather, it means that the preferred product symmetry is a consequence of a steric effect that favors  $\text{Ar}^*$  approach in the plane of rotation of the  $\text{N}_2$ , with the  $p$  orbital also in this plane. As discussed by Stedman and Setser,<sup>52</sup> the reason for such a restrictive condition must lie in the orbital overlap requirements and in the anisotropy of the potential energy surface.

The orbital overlap requirements can be visualized by considering an  $\text{N}_2$  molecule rotating in the plane of symmetry of the right-hand  $\pi$  orbitals in Fig. 2 and the  $\text{Ar}^*$  approaching in this same plane. The right  $\pi$  orbitals are then  $\pi^+$  and the left are  $\pi^-$  with respect to the plane of rotation. The sets of orbitals that must overlap in order for the reaction to occur are the  $(3p + 4\sigma_u)$  and the  $(4s + 2\pi_g)$ . The first pair are tightly bound orbitals, and the second pair are loosely bound, so we expect the overlap requirement to be more restrictive for the first pair. The  $4\sigma_u$  is an inner antibonding or “lone pair” type of orbital with the electron density concentrated at the ends of the molecule, where it is not “protected” (in a potential energy sense) by the double  $\pi$  bond. Therefore, the doubly colinear approach (with the half-filled  $\text{Ar}^* 3p$  orbital aligned with the  $\text{N}_2$  bond) will maximize the overlap of the  $4\sigma_u$  and  $3p$  orbitals, and this is expected (aside from other factors) to maximize the rate of the electron transition to the intermediate potential. Overlap of the second orbital pair, while not so restrictive, is favored by a bent configuration, which requires trajectories that approach at some intermediate angle, or that sample a range of angles. (This can be seen by superposing the  $4\sigma_u$  and  $2\pi_g$  orbitals of Fig. 2.) In imagining such trajectories it is instructive to consider the relative speed of the translational vs the rotational motion. At room temperature the average  $\text{N}_2$  rotational frequency is about  $1.2 \times 10^{12} \text{ s}^{-1}$  and the average  $\text{Ar}^* + \text{N}_2$  relative velocity is about  $6.7 \times 10^{12} \text{ \AA s}^{-1}$ , giving about 6  $\text{\AA}$ /revolution. Thus the configuration will change from linear to bent (or vice versa) during a typical collision

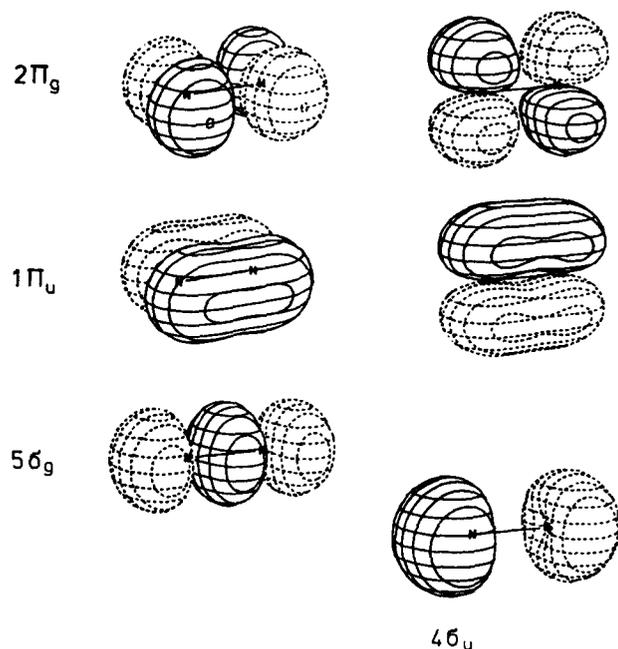


FIG. 2. Three-dimensional drawings of the relevant valence molecular orbitals of  $\text{N}_2$  (from Ref. 56). Full contours correspond to positive amplitudes and dotted contours to negative amplitudes.

in the  $\text{N}_2$  rotation plane.

The above considerations rationalize the Setser model in terms of orbital overlap arguments. There are several reasons for assuming that the reaction takes place via two 1-electron transitions, i.e., through an intermediate state; one is that since the  $(\text{Ar}^+ + \text{N}_2^-)$  and  $(\text{Ar}^- + \text{N}_2^+)$  Coulomb potentials fall into the range of the  $(\text{Ar}^* + \text{N}_2)$  potential at about 3 Å, such a state is probably energetically accessible.<sup>51,52</sup> The cross section behavior indicates that the reaction occurs via a repulsive interaction, and so the electronic transitions take place at close range. A second reason is the likelihood that two 1-electron transitions provide a faster path for reaction than a 2-electron transition. A third factor is that two 1-electron transitions permit motion in the collision complex to facilitate the reaction, as described above. Another is that Gislason *et al.*<sup>51</sup> found that an intermediate state model gave good agreement with the vibrational data. Finally, we note that an intermediate state with a considerable degree of charge transfer in the direction  $\text{K}^+ \text{N}_2^-$  is generally believed to account for interactions of  $\text{K} + \text{N}_2$ .<sup>57</sup>  $\text{Ar}^*$  is the chemical analog of K, since both have a single unpaired 4s outer electron. The ionization potentials are 4.21 eV for  $\text{Ar}(^3P_2)$  vs 4.34 eV for K, so intermediate formation with  $\text{Ar}(^3P_2)$  is expected to be as favorable as with K.

Sadeghi and co-workers<sup>31</sup> disagreed with the model of Setser and co-workers on the basis that their symmetry argument neglects the spin-orbit interaction which the spectra show to be very effective, and in addition the symmetry arguments do not hold for  $\text{Ar}(^3P_0)$ , which they observed to also favor  $\pi^+$  formation. They found the more quantitative plane-of-symmetry model of Ochkin *et al.*<sup>58</sup> to be unsatisfactory for the same reason, as well as the fact that the predicted  $\Lambda$ -doublet intensities are not in agreement with experiment. They pointed out that in order to obtain the high product rotational states which are observed and also conserve angular momentum, it is necessary for the final relative angular momentum of  $\text{Ar} + \text{N}_2(C)$  to be roughly antiparallel to the  $\text{N}_2(C)$  rotational angular momentum. This means that the Ar tends to leave in the  $\text{N}_2(C)$  rotation plane, and from the kinematics it also means that the Ar tends to be back-scattered, as found by Winiicur and Fraites.<sup>34</sup> Because of the spin-orbit interaction, Sadeghi and co-workers used a model in which the symmetry of the electronic wave function is not conserved separately for orbital and spin coordinates, but only for both together. They assumed that the total electronic Hamiltonian has  $+$  symmetry with respect to the complex plane, and then obtained the propensity rules for the fine structure states from symmetry arguments. However, conservation of symmetry alone was not sufficient to account for the anomalously strong  $\pi^+$  preference. To explain this, they postulated that it is due to orientation of the  $2\pi_g$  orbital by the final state interaction with the departing  $\text{Ar}(^1S_0)$  atom.

Sadeghi and co-workers used a model with two adjustable parameters to fit their observed fine structure intensities;  $p$  is the probability that starting with any trajectory the overall symmetry of the initial state wave function with respect to the complex plane is transferred to  $\text{N}_2(C)$ , and  $k^+$  is the additional propensity factor favoring  $\pi^+$  formation. The

parameter  $p$  is a measure of the correlation between the complex plane and the  $\text{N}_2(C)$  rotation plane, i.e., it is unity when they coincide and 0.5 for no correlation. The values which gave the best fit to the data were  $p = 0.75$  and  $k^+ = 3$ , so the average correlation between the two planes is about halfway between coplanar and random, and  $\pi^+$  is favored by a factor of 3 over  $\pi^-$ .

We have already suggested above that with the Setser model, the  $\pi^+$  propensity is a consequence of orbital overlap rather than symmetry. This viewpoint reconciles the Setser and Sadeghi models. In the Setser model the *initial state* orbital overlap requirements (aided by the interaction potential) select reaction trajectories which give  $2\pi_g$  orbitals oriented in the  $\text{N}_2$  rotation plane. In the Sadeghi model the kinematics result in exit trajectories which, due to the *final state* interaction, orient the  $2\pi_g$  orbital. This argument implies that the orientation is caused by the van der Waals forces, after the final electronic transition has occurred. These two mechanisms are not inconsistent and, in principle, both of them could contribute to the  $\pi^+$  propensity.

#### 4. Application of the models to the alignment and $\pi^+$ propensity results

We first consider the implications of the reaction cross section behavior combined with the Setser model. According to the model, the reaction requires the overlap of two tightly bound directional orbitals. From the cross section behavior, it appears that at low velocities this only happens for nearly colinear collisions, giving a small cross section and backscattering of the products. As the velocity is increased the interpenetration and perturbation of the orbitals increases, which relaxes the steric requirement, and the cross section increases. Other factors are also expected to play a role, i.e., the anisotropy of the potential surface and the density of states of the collision complex. At about 250 meV the cross section levels off and at higher energies it slowly decreases. This may be related to the Landau-Zener picture, but it could also involve the electronic state lifetime, i.e., the degree of further penetration of the orbitals on the repulsive wall is more than compensated by the decreasing collision time.

The  $\text{Ar}^* + \text{N}_2(C)$  cross section increases by a factor of 3 from 40 to 250 meV, yet the alignment shows little evidence of this change. From consideration of the line-of-centers energy requirement for a repulsive-type reaction, the cross section increase is expected to be accompanied by an increase in the average reactive impact parameter. Rotational excitation of the  $\text{N}_2(C)$  is caused both by the exoergicity of the reaction (coupled with translational recoil) and by translational-to-rotational energy transfer in the reactive collisions. Of course, the motion on the potential energy surface involves both kinds of rotational excitation together, but we can distinguish them for the purpose of discussion and refer to these two types of rotational excitations and their corresponding alignments as “recoil” and “T/R” (for translational-to-rotational), respectively.

The results in Fig. 1 can be explained as the result of two opposing trends. The reaction favors molecules that happen

to be rotating in planes through the relative velocity vector, so the reactants are preselected for positive alignment. To the extent that the plane of rotation is conserved during the reaction, this alignment is carried over to the products. (The direction of the rotational angular momentum vector is in general reversed by the reaction and, of course, its magnitude is also changed.) Thus the positive recoil alignment persists down to the lowest average collision energy studied in this work and the model predicts that it will persist down to zero energy. However, because the steric effect is expected to decrease with increasing energy, the recoil alignment should also decrease with energy.

The T/R alignment approaches zero at zero energy and is expected to increase monotonically with energy in our energy range. The positive slope in Fig. 1 indicates that the increasing T/R alignment more than compensates for the decreasing recoil alignment with increasing energy. The fact that the resultant  $A$  increases nearly linearly with energy over the range studied may be fortuitous; further studies at higher and lower energies would be useful to explore this question.

It is of interest to compare the implications of the Sadeghi model vs the Setser model with regard to the velocity ( $k$ ) dependence of  $A = -2\langle P_2(\hat{J} \cdot \hat{k}) \rangle$  and the  $\pi^+$  propensity factor  $k^+$ .<sup>31</sup> The Sadeghi model does not have a steric effect in the entrance channel, and so it does not predict any dynamic correlation between  $\hat{J}'$  and  $\hat{k}$ . Therefore  $A$  is expected to be zero at  $k = 0$  and to increase with velocity due to T/R alignment. Since the Setser model predicts a positive  $A$  at  $k = 0$ , and our data indicate a positive intercept rather than a trend to zero, we take this as tentative evidence in support of the Setser model.

The  $\pi^+$  propensity of  $k^+ = 3$  is an experimentally derived quantity and applies to both models. In the Sadeghi model  $k^+$  will have a positive value  $k_0^+$  at zero collision velocity and will tend to increase with velocity due to T-R alignment. In contrast, in the Setser model we expect  $k^+$  to be a maximum at zero velocity and to decrease with increasing velocity for the same reason that the recoil alignment decreases; in the Setser model,  $k^+$  is not correlated with T/R alignment. Thus the two models predict opposite trends for the velocity dependence of the  $\pi^+$  propensity.

#### IV. SUMMARY

In this work we have studied the fluorescence polarization from the  $\text{Ar}^* + \text{N}_2$  excitation transfer reaction giving  $\text{N}_2(C^3\Pi_u)$ , and that from four dissociative excitation reactions, as a function of collision velocity. The three dissociative excitation cases with perpendicular-type transitions gave average polarization quotients  $\bar{Q} = -0.011 \pm 0.01$  and the  $Q$  values were found to be independent of velocity. This shows that  $Q = -0.011$  was the zero offset in these experiments and that with effusive beam time-of-flight conditions and a dual optical system we can experimentally measure the  $Q = 0$  base line to an accuracy of  $\pm 0.01$ , which is 1% of the value of  $Q$  in the kinematic limit ( $\hat{J}' \perp \hat{k}, \hat{k} \parallel \hat{z}$ ). The dissociative excitation of  $\text{BrCN}$  by  $\text{Xe}^*$ , in which  $\text{CN}^*$  fluoresces by a parallel-type transition, was found to give essentially no alignment of the CN.

The  $\text{N}_2(C)$  alignment  $A$  was found to increase nearly linearly with collision energy over the range 42–463 meV. The observed range of alignments corresponds to a range of characteristic angles  $\theta_c$  between  $\hat{J}'$  and  $\hat{k}$  from  $3.6^\circ \pm 0.2^\circ$  to  $5.1^\circ \pm 0.2^\circ$  above the isotropic value of  $54.7^\circ$ , where the error limits are derived from the  $A$  error limits. The limits include uncertainty in the  $Q = 0$  base line and the statistical error, but not a calibration of the absolute value of  $Q$ . Evidence is cited which indicates that the absolute accuracy of  $Q$  is 10% or better, but further experiments will be required to confirm this. With the use of calibration techniques, the dual optical system method used in this work should be capable of measuring the absolute polarization of the products to within a few percent. In the  $A$  range of the present work, this corresponds to a few tenths of a degree in  $\theta_c$ . Methods using a single phototube and a rotating polarizer should be capable of obtaining even better accuracy. This illustrates that fluorescence polarization measurements can be an extremely sensitive probe of the reaction dynamics.

We have reviewed the copious information on the  $\text{Ar}^* + \text{N}_2$  reaction and the models that have been used to explain it. We conclude that the model which best fits all the data is one in which the reaction takes place preferentially in the plane of rotation of the  $\text{N}_2$ . The probable reason for this is that the resulting trajectories give more favorable overlaps of the  $\text{Ar}^* 3p$  orbital with the  $\text{N}_2 4\sigma_u$  orbital and the  $\text{Ar}^* 4s$  orbital with the  $\text{N}_2 2\pi_g$  orbital, which are required for the exchange electron transitions to take place. It is likely that the reaction occurs via an intermediate state, i.e., that the two electronic transitions occur sequentially in the collision complex.

The alignment of  $\text{N}_2(C)$  increases fractionally by only about a tenth as much as the reaction cross section in the range 42–250 meV. We attribute the gradualness of the change in alignment to two effects with opposite velocity dependences; the recoil alignment and the translational-to-rotational energy transfer (T/R) alignment. The T/R alignment is expected to increase with collision velocity. The recoil alignment is produced by the exoergicity of the reaction combined with the steric effect and is expected to decrease with velocity as the steric effect decreases. In principle, the recoil alignment should persist down to zero velocity, as suggested by extrapolation of the present data.

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#### APPENDIX: FLUORESCENCE POLARIZATION AND ROTATIONAL ALIGNMENT FROM PARALLEL AND PERPENDICULAR ELECTRONIC TRANSITIONS

The basic experimental and calculated quantities in studies of rotational alignment by fluorescence polarization

are the intensities of the light polarized parallel and perpendicular to the average relative velocity vector ( $I_{\parallel}$  and  $I_{\perp}$ ) and the function  $\langle \cos^2 \theta \rangle = \langle (\hat{J}' \cdot \hat{k})^2 \rangle$ , where  $\hat{J}'$  is the rotational angular momentum unit vector and  $\hat{k}$  is the relative velocity unit vector. The “degree of polarization” and the “degree of alignment” have been expressed in terms of several different parameters by different groups and it may be useful to the general reader to give these here with their limits, as is done in Table II. The alignment has usually been expressed in terms of function 1 or 2. We used function 3 previously<sup>19</sup> for convenient plotting of the alignment with the polarization  $P$  (function 5), but in retrospect this was an inelegant choice.

The choice of which form to use is arbitrary. However, in the absence of other criteria, we prefer an alignment function with integer limits. In particular, it is useful to have a value of unity in the kinematic limit ( $\hat{J}' \perp \hat{k}$ ) since this provides a convenient and physically intuitive reference scale for comparing and interpreting alignment data. In the present paper we have expressed the alignment as  $A = -2\langle P_2(\hat{J}' \cdot \hat{k}) \rangle$  because it is the simplest function that satisfies these criteria. Having chosen this function, it is then desirable to express the polarization in terms of the same laboratory function, i.e.,  $-2\langle P_2(\hat{J}' \cdot \hat{z}) \rangle$ , so that in beam-gas studies the polarization and the alignment can be directly compared on the same plot. From Eq. (4), the ratio of these

TABLE II. Comparison of alignment and polarization functions for electric dipole transitions in linear molecules.

Function	Limits <sup>a</sup>	
	$J'_{\parallel}$	$J'_{\perp}$
1. $\langle P_2(\hat{J}' \cdot \hat{k}) \rangle = 1/2 [3\langle (\hat{J}' \cdot \hat{k})^2 \rangle - 1]$	1	-1/2
2. $\alpha = a_2/a_0 = 5\langle P_2(\hat{J}' \cdot \hat{k}) \rangle^b$	5	-5/2
3. $-2/3 \langle P_2(\hat{J}' \cdot \hat{k}) \rangle^c$	-2/3	1/3
4. $A = -2\langle P_2(\hat{J}' \cdot \hat{k}) \rangle^d$	-2	1
5. $P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{-3\langle P_2(\hat{J}' \cdot \hat{z}) \rangle}{4 - \langle P_2(\hat{J}' \cdot \hat{z}) \rangle}$	-1	1/3
6. $P_q = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3\langle P_2(\hat{J}' \cdot \hat{z}) \rangle^e}{2 + \langle P_2(\hat{J}' \cdot \hat{z}) \rangle}$	1	-1
7. $R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = -1/2 \langle P_2(\hat{J}' \cdot \hat{z}) \rangle$	-1/2	1/4
8. $R_q = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \langle P_2(\hat{J}' \cdot \hat{z}) \rangle^e$	1	-1/2
9. $Q = 4R = -2\langle P_2(\hat{J}' \cdot \hat{z}) \rangle^f$	-2	1
10. $Q_q = -2R_q = -2\langle P_2(\hat{J}' \cdot \hat{z}) \rangle^e$	-2	1

<sup>a</sup> The limits are for  $\hat{J}'$  parallel or perpendicular to either  $\hat{k}$  (alignment) or  $\hat{z}$  (polarization).

<sup>b</sup>  $a_0$  and  $a_2$  are the Legendre expansion coefficients (Ref. 6).

<sup>c</sup> Alignment parameter used in our previous work (Ref. 19).

<sup>d</sup> Alignment parameter used in this work.

<sup>e</sup> Applies to the  $Q$ -branch lines in perpendicular-type transitions.

<sup>f</sup> Polarization quotient used in this work.

two functions gives the kinematic blurring factor  $\langle P_2(\hat{k} \cdot \hat{z}) \rangle$ .

In Table II, the polarization functions  $P$  and  $R$  both apply to both the  $P$ -branch and  $R$ -branch lines (there is a coincidence of nomenclature here), whereas the functions which we have labeled  $P_q$  and  $R_q$  apply to the  $Q$ -branch lines. This has been discussed by Zare and Simons and co-workers.<sup>6,14</sup> In parallel-type transitions the electric transition dipole  $\bar{\mu}$  lies along the internuclear axis and  $Q$ -branch transitions ( $\Delta J = 0$ ) are not allowed. In perpendicular-type transitions  $\bar{\mu}$  is perpendicular to the internuclear axis, but can lie either in the plane of rotation or perpendicular to this plane; the former orientation gives the  $P$ -branch and  $R$ -branch lines and the latter the  $Q$ -branch lines. (Since the polarization is averaged over the rotational motion of the molecule, it is obvious that it is the same for parallel and perpendicular orientations of  $\bar{\mu}$  within this plane.)

As can be seen in Table II,  $2R + R_q = 0$ , so for a perpendicular-type transition with equal  $P$ -,  $Q$ -, and  $R$ -branch intensities the overall fluorescence polarization will be zero, regardless of the alignment. However, the alignment can be obtained if it is possible to measure the polarization of the resolved  $P$ -,  $Q$ -, or  $R$ -branch lines. The reason that the  $Q$ -branch polarization is twice as strong and opposite in sign to that of the  $P$ - and  $R$ -branches is that  $\hat{u}_q$  is orthogonal to  $\hat{u}_{p,r}$  and does not rotate with the molecule. The  $R_q$  limits correspond to  $\hat{u}_q \parallel \hat{z}$  ( $R_q = 1$ ) and  $\hat{u}_q \perp \hat{z}$  ( $R_q = -1/2$ ). The  $R = -1/2$  limit also corresponds to  $\hat{u}_{p,r} \perp \hat{z}$ , but the  $R = 1/4$  limit corresponds to  $\hat{u}_{p,r}$  rotating in all planes through  $\hat{z}$ . If  $x$  is the axis of observation,  $R = 0$  for rotation in the  $y$ - $z$  plane, and  $R = 1$  for rotation in the  $x$ - $z$  plane; the average over all azimuthal planes is  $1/4$ .

The polarization functions that we need to match the alignment function  $A$  are given in terms of  $R$  and  $R_q$ .<sup>14</sup> For the  $P$ - and  $R$ -branch lines  $-2\langle P_2(\hat{J}' \cdot \hat{z}) \rangle = 4R$  and for the  $Q$ -branch lines this function is given by  $-2R_q$ . Thus  $A$ ,  $4R$ , and  $-2R_q$  all have the same functional form and provide a convenient set of functions that approach unity in the kinematic limit ( $\hat{J}' \perp \hat{k}$ ,  $\hat{k} \parallel \hat{z}$ ) and  $-2$  in the antikinematic limit ( $\hat{J}' \parallel \hat{k}$ ,  $\hat{k} \parallel \hat{z}$ ). Therefore in Table II we have defined the “polarization quotients” as  $Q = 4R$  for  $P$ - and  $R$ -branch lines and  $Q_q = -2R_q$  for  $Q$ -branch lines.

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