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ELECTRONIC ANGULAR MOMENTUM TRANSFER IN THE
I(DOUBLET $P(\frac{1}{2})$) + NF (A SINGLET DELTA) SYSTEM

AEROSPACE CORPORATION

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Electronic Angular Momentum Transfer in the

$$I(^2P_{1/2}) + NF(a^1\Delta) \text{ System}$$

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A rate coefficient at 298 K of $>2.6 \times 10^{14} \text{ cm}^3 \text{ -mol}^{-1} \text{ -sec}^{-1}$ has been deduced for the electronic energy transfer: $I(^2P_{1/2}) + NF(a^1\Delta) \rightarrow I(^2P_{3/2}) + NF(b^1\Sigma^+)$		

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This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER

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PREFACE

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PREFACE 1

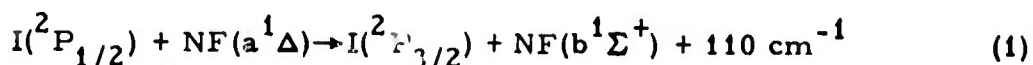
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ELECTRONIC ANGULAR MOMENTUM TRANSFER IN THE
 $I(^2P_{1/2}) + NF(a^1\Delta)$ SYSTEM

Evidence has been observed for a nearly gaskinetic rate coefficient for the E-E transfer:



by using the large-diameter, medium-pressure flow tube facility.¹ Such a large rate coefficient had been anticipated by previous studies^{*,**,2} that describe the role of electronic spin conservation in the reactive $F + H_2 / H + NF_2$ systems in producing NF electronically excited species.^{**,2} The experiment involves determination of the axial variations of $NF(a^1\Delta)$ and $NF(b^1\Sigma^+)$ number densities in a sequence of carefully selected reagent flow conditions. This is followed by observation of the $(a^1\Delta - X^3\Sigma^-)$ and $(b^1\Sigma^+ - X^3\Sigma^-)$ spontaneous emissions in the axially translating reaction zone. The enhancement of $NF(b^1\Sigma^+)$ by the presence of $I(^2P_{1/2})$ can then be observed, and an estimate can be made of the rate coefficient by using a chemical kinetic model that fits the experimental number densities.

From the passage of $Ar + NF_3$ through an rf discharge, F and 1% NF_2 are produced, which can be reacted with D_2 and HI injected rapidly into the principal flow from an axially movable tee injector located on the tube centerline. The reaction $F + D_2$ yields D atoms in excess, which, in turn, react with NF_2 to predominantly produce² $NF(a^1\Delta)$. The excess D also rapidly

* J. M. Herbelin, "The Role of Electron Spin in the NF System," to be published.

** M. A. Kwok, J. M. Herbelin, and N. Cohen "Collisional Quenching and Radiative Decay Studies of $NF(a^1\Delta)$ and $NF(b^1\Sigma^+)$," to be published.

¹ Munson A. Kwok and Roger L. Wilkins, J. Chem. Phys. 63, 2453 (1975).

² J. M. Herbelin and N. Cohen, Chem. Phys. Lett. 20, 605 (1973).

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reacts with HI to produce mainly $I(^2P_{3/2})$ atoms.^{3,4} In order to generate sufficient $I(^2P_{1/2})$, it is necessary to pass O_2 through a 2.45 GHz microwave cavity some distance upstream of the reaction zone to yield $O_2(a^1\Delta)$. The O atoms are suppressed by the heated mercuric oxide coating in the quartz sidearm. The transfer $O_2(a^1\Delta) + I(^2P_{3/2})$ is known to be extremely rapid⁵ for the efficient production of $I(^2P_{1/2})$.

Flow conditions are chosen such that $O_2(a^1\Delta)$ is excess to I for ease of analysis, but not in sufficient excess to obliterate evidence of the $I(^2P_{1/2}) + NF(a^1\Delta)$ transfer by the alternative process² $O_2(a^1\Delta) + NF(a^1\Delta)$. Typical reagent flowrates for Case 4 in Fig. 1 would be in $\mu\text{mol}\cdot\text{sec}^{-1}$: F, 15; NF_2 , 0.15; O_2 , 50; D_2 , 150; HI, 0.08. Experience^{6,7} indicates that the amount of $O_2(a^1\Delta)$ generated in the usual 2.45 GHz 70 W microwave is 5% of O_2 . The tube operates at 1 Torr, 298 K and 6800 cm sec^{-1} . Case 1 is a previously used baseline.² Cases 2 and 3 verify the necessity of the simultaneous presence, in Case 4, of $O_2(a^1\Delta)$ and I for significant pumping of $NF(b^1\Sigma^+)$. The axial number density plot of $NF(b^1\Sigma^+)$ versus Z shown in Fig. 1 for Case 4 shows this strong pumping. We interpret Case 4 to mean that $I(^2P_{1/2})$ is rapidly produced with the presence of $O_2(a^1\Delta)$ and then rapid transfer occurs, as described by Eq. (1). Axial number density plots of $NF(a^1\Delta)$ for Cases 1 through 4 are virtually identical. $NF(a^1\Delta)$ behaves as a reservoir because, in all cases, the $NF(b^1\Sigma^+)$ is at most only 1% of observed $NF(a^1\Delta)$ concentrations.

A quantitative estimate of the transfer rate coefficient for Eq. (1) can be made. The growth of $NF(b^1\Sigma^+)$ for Case 4 in Fig. 1 is found to be quadratic in Z (or time). This implies that either $NF(a^1\Delta)$ or $I(^2P_{1/2})$ is in a

³W. E. Jones, S. D. MacKnight, and Lo Teng, Chem. Rev. 73, 407 (1973).

⁴P. Cadman and J. C. Polanyi, J. Phys. Chem. 72, 3715 (1968).

⁵R. G. Derwent and B. A. Thrush, Chem. Soc. Faraday Disc. 53, 162 (1972).

⁶R. G. Derwent and B. A. Thrush, Trans. Faraday Soc. 67, 2036 (1971).

⁷L. W. Bader and E. A. Ogryzlo, Disc. Faraday Soc. 37, 46 (1964).

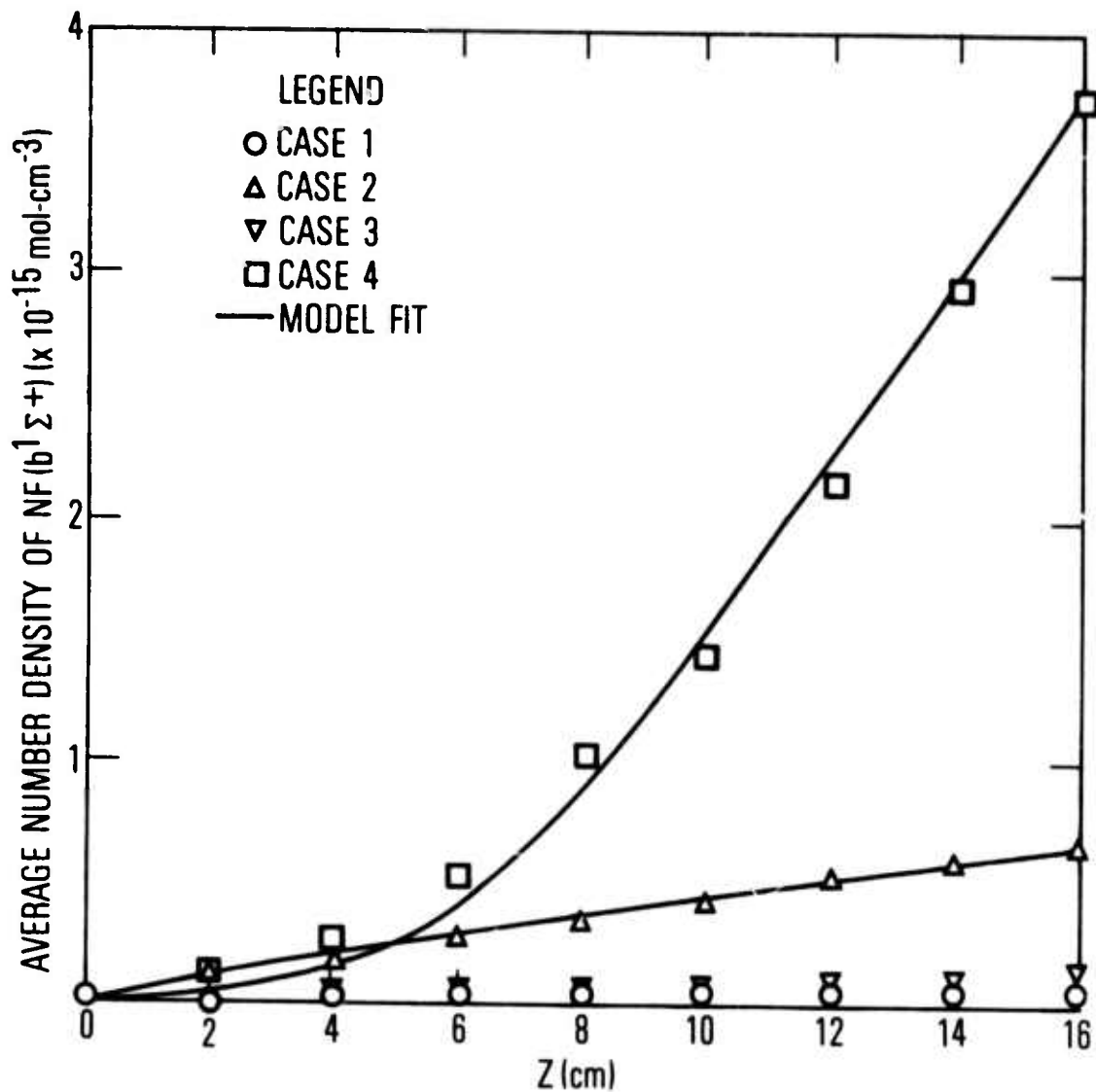


Figure 1. Axial Variations of the Number Density of $NF(b^1\Sigma^+)$, Averaged Along the Tube Diameter. Case 1: F, NF_2 , D_2 , O_2 . Case 2: F, NF_2 , D_2 , O_2 , $O_2(a^1\Delta)$. Case 3: F, NF_2 , D_2 , O_2 , HI. Case 4: F, NF_2 , D_2 , O_2 , $O_2(a^1\Delta)$, HI. The solid lines represent model fits.

linear region of growth. A simple five-kinetic equation analysis for the one unknown rate shows that the lower bound for k_1 , in Eq. (1), is 2.6×10^{14} $\text{cm}^3 \text{mol}^{-1} \text{sec}^{-1}$. The estimate is a bound because the absolute $\text{O}_2(a^1\Delta)$ density has not been measured but has been assumed to be $\leq 5\%$ of O_2 , and k_1 is inversely proportional to $\text{O}_2(a^1\Delta)$. A more detailed description of this study will be given elsewhere.

LABORATORY OPERATIONS

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