DEPENDENCE OF PRODUCT ALIGNMENT ON PRODUCT VIBRATION FOR THE Ca + F_2 CHEMILUMINESCENT REACTION

M.G. PRISANT, C.T. RETTNER and R.N. ZARE

Department of Chemistry, Stanford University, Stanford, California 94305, USA

Received 4 March 1982

The product polarization for the beam–gas chemiluminescent reaction $Ca(^1S_0) + F_2 \rightarrow CaF(B\,^2\Sigma^+) + F$ is found to be vary by more than a factor of two over the B–X band system. This reveals a strong dependence of CaF(B) state alignment on vibrational level.

1. Introduction

To follow the consequences of the conservation of energy in reactive scattering, experiments need only determine scalar quantities: rate constants, cross sections as a function of velocity, product state distributions, etc. [1]. To follow the consequences of the conservation of momentum demands, in addition, analysis of vector quantities having both magnitude and direction [2,3]. To date such studies have emphasized the determination of product angular distributions, i.e. the relation of product *orbital* angular momentum to reagent relative velocity [4]. In this paper we examine a less widely studied vector quantity: the partitioning of total angular momentum into *internal* angular momentum of products.

Our experiments use the technique of chemiluminescence polarization measurements to assess product rotational alignment about $\hat{k}$, the initial relative velocity vector [5–8]. If $\hat{J}'$ is the direction of the product internal angular momentum, the rotational alignment in the center-of-mass frame is defined as

$$\langle P_2(\hat{J}' \cdot \hat{k})\rangle \equiv \tfrac{1}{2}(3\langle\cos^2\chi\rangle - 1), \qquad (1)$$

with ⟨ ⟩ denoting the ensemble average and χ the angle between $\hat{J}'$ and $\hat{k}$. A previous publication [6] develops the procedure to extract this quantity from beam–gas chemiluminescence polarization measurements. The polarization of discrete features of the dispersed chemiluminescence can yield the rotational alignment of individual product vibrational states. In the absence of kinematic constraints imposed by the relative masses of the reagents, this detailed information severely tests models of the reaction dynamics [2,6,9].

Here we present a study of the chemiluminescent reaction [10,11]

$$Ca(^1S_0) + F_2 \rightarrow CaF(B\,^2\Sigma^+) + F. \qquad (2)$$

This system was chosen for three reasons. First, the CaF $B\,^2\Sigma^+ - X\,^2\Sigma^+$ emission stems from a parallel-type transition, allowing product alignment to be determined in the absence of rotational resolution [6]. Second, the reaction is highly exoergic, permitting product alignment to be determined over an energy range of ≈160 kJ $mole^{-1}$, corresponding to ≈27 vibrational levels [11]. Third, the mass of the departing F atom allows it to carry off considerable orbital angular momentum; hence product rotational alignment is in no way constrained by kinematics.

2. Experimental

A schematic of the beam–gas apparatus employed is given in fig. 1. The calcium beam source resembles that described previously [5,12]. A resistively heated graphite tube maintains a graphite oven at 1200 K in a differentially pumped chamber.

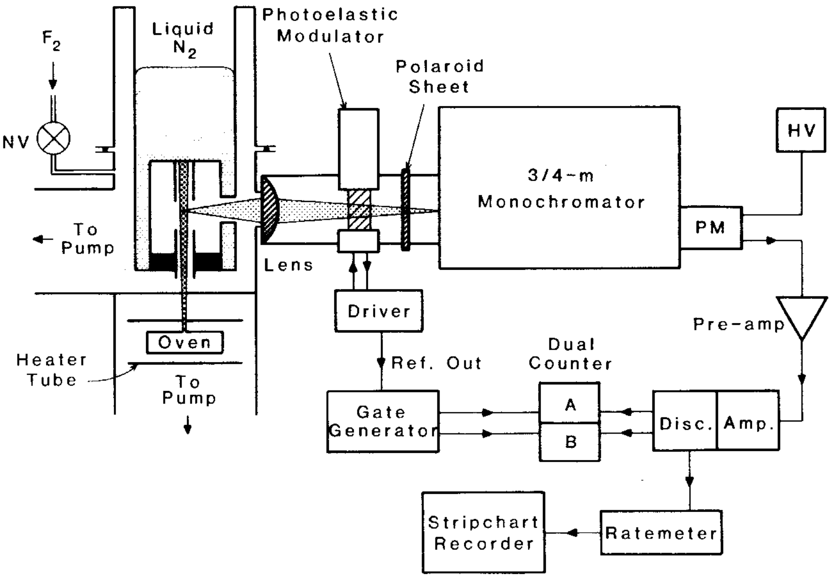

Fig. 1. Arrangement for polarization measurements of resolved beam–gas chemiluminescence.

Under normal conditions there are no metastables in the beam. However, application of a small voltage between the (1 mm) oven orifice and the surrounding heater tube produces a metastable discharge and the metastable species are readily detected by monitoring atomic emission. Fluorine gas (Matheson) is passed through a NaF trap to remove any HF present and enters the reaction chamber through a monel needle valve (Granville–Phillips model 203-015). The F_2 pressure is held at $\approx 1 \times 10^{-4}$ Torr. The gas temperatures may be either ambient (295 K) or $\approx$77 K, maintained by a liquid-nitrogen-filled copper shroud which almost completely surrounds ($\approx$11 sr) the reaction zone.

A single 8 cm focal length lens images the chemiluminescence onto the slits of a $\frac{3}{4}$ m monochromator (Spex 1702). The dispersed emission is detected by a cooled photomultiplier tube. Both chemiluminescence spectra and polarization ratios are recorded using pulse counting techniques. Spectra are obtained by feeding the amplified and discriminated photomultiplier output to a ratemeter, which in turn drives a stripchart recorder.

Polarization ratios are determined with the aid of a photoelastic modulator (Hinds International, PEM-3) and a sheet polarizer (Polaroid HN38) [13]. The PEM houses a vibrating calcium fluoride crystal. This device is placed at the entrance slit of the monochromator in front of the sheet polarizer, which is aligned to transmit light polarized parallel to the calcium beam axis (see fig. 1). At minimum compression the crystal transmits light without retardation and the system passes incident light polarized parallel to the beam axis. At maximum compression the crystal retards light by $\lambda/2$ and the system now passes incident light polarized perpendicular to the beam axis. By gating two counters to sample at the minimum and maximum compression points, we simultaneously measure the intensities of the parallel ($I_\parallel$) and perpendicular ($I_\perp$) polarization components of the chemiluminescence. The degree of polarization is:

$$P \equiv (I_\parallel - I_\perp)/(I_\parallel + I_\perp). \tag{3}$$

We have calibrated this polarimeter with fully polarized light using a sheet polarizer and with unpolarized light using the 657.3 nm metastable emission, Ca $^1S_0 \leftarrow {}^3P_1$.

3. Results

Fig. 2a presents the CaF $B\,^2\Sigma^+ - X\,^2\Sigma^+$ chemi-

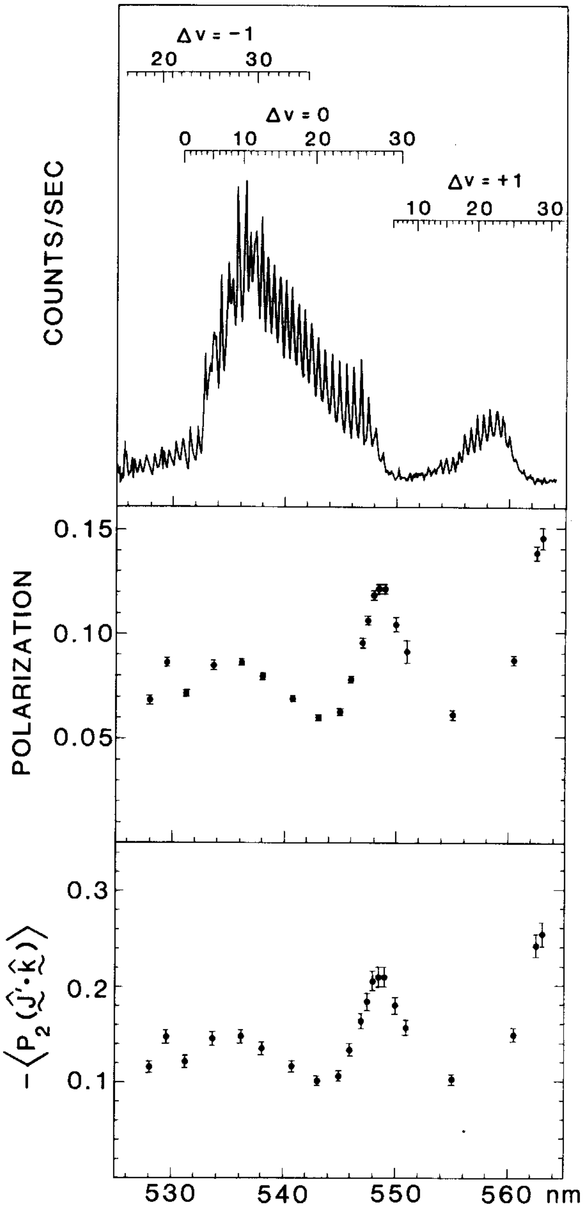

Fig. 2. Plot of (a) the Ca + F_2 chemiluminescence spectrum, (b) the CaF($B\,^2\Sigma^+$) product polarization and (c) the CaF($B\,^2\Sigma^+$) product alignment in the center of mass as a function of wavelength. The band origin positions of each Δv sequence are indicated, but do not imply an assignment of the observed features in (a). Nearly identical rotational constants for the X and B states cause bandheads to appear up to 1.5 nm to the red of the band origins [14].

luminescence spectrum obtained for room-temperature F_2 and with an oven temperature of 1200 K ‡. The spectrum was recorded at a resolution of 0.1 nm, providing peak count rates of $\approx 10^3$ s^{-1}. The $\Delta v = 0$ and ±1 sequences are shown. Bandheads are formed in the R_1 and R_2 branches while the P_1 and P_2 branches contribute to the underlying background. Though complete assignment awaits a full analysis, band origins are shown to suggest the identification of spectral features. The Franck–Condon factors for this system allow us to see emission in the $\Delta v = \pm 1$ sequences only for high vibrational levels [11,14]. Cooling the F_2 gas to 77 K served to slightly decrease the relative intensity of the long-wavelength tail at $\approx$550 nm.

Fig. 2b shows the degree of polarization of the chemiluminescence as a function of wavelength. Each point was obtained with a bandpass of 0.5 nm. Error bars reflect the total number of counts accumulated for each measurement. Polarization values display a marked variation with wavelength. At lower vibrational levels, CaF(B) product becomes slightly more depolarized with increasing vibrational energy. This trend reverses at higher vibrational levels and polarization begins to rapidly increase with increasing vibrational energy. The pattern is duplicated in both vibrational sequences.

4. Discussion

Center-of-mass product alignment $\langle P_2(\hat{J}' \cdot \hat{k})\rangle$ may be extracted from a polarization measurement. For a parallel-type transition we obtain from ref. [6]

$$\langle P_2(\hat{J}' \cdot \hat{k})\rangle = \frac{4P}{P-3}\,\frac{1}{\langle P_2(\hat{k} \cdot \hat{Z})\rangle}\,, \qquad (4)$$

where the term $\langle P_2(\hat{k} \cdot \hat{Z})\rangle^{-1}$ properly accounts for the beam–gas averaging, with Z along the beam axis. This factor depends only on the masses and temperatures of the beam and gas species through one-reduced parameter. The values of $\langle P_2(\hat{k} \cdot \hat{Z})\rangle$ have been

---

‡ Introduction of metastables into the beam served to slightly decrease the chemiluminescence intensity but did not noticeably change the observed spectrum. This is contrary to the observations reported in ref. [11].

tabulated elsewhere [6]. Eq. (4) permits us to transform the chemiluminescence polarizations displayed in fig. 2b to center-of-mass alignments, presented in fig. 2c. Clearly the CaF(B) alignment depends strongly on its vibrational state. Indeed the value of $\langle P_2(\hat{J}' \,|\hat{k})\rangle$ changes by more than a factor of two over the wavelength range of the B–X $\Delta v = 0, \pm 1$ band sequences.

Although the $Ca + F_2$ chemiluminescent reaction is not kinematically constrained, we have observed that the $CaF(B\,^2\Sigma^+)$ product is significantly aligned. Indeed, our alignment when averaged over all vibrational levels, $\langle P_2(\hat{J}' \cdot \hat{k})\rangle_{av} = -0.14 \pm 0.01$, might be compared to the value of −0.12 for $K + Br_2$ from electric deflection measurements [15] and −0.12 for $Xe^{(m)} + Br^2$ from crossed beam chemiluminescence studies [8]. Note that all three of these reactions are thought to proceed by an electron jump mechanism [2]. However, the present study unmasks for the first time the dependence of the alignment on product vibration.

It is common to imagine that the total energy released, E_{tot}, in a bimolecular exchange reaction, $A + BC \rightarrow AB + C$, can be divided into repulsive and attractive components, denoted by $\mathscr{A}$ and $\mathscr{R}$, respectively [16]. Let $\mathscr{A}$ be the energy released along the A–B product coordinate and let $\mathscr{R}$ be the energy along the B–C reagent coordinate. In this conceptual framework $\mathscr{A}$, which equals $E_{tot} - \mathscr{R}$, appears largely as product vibration. Because $\mathscr{A}$ is directed along the product coordinate, it cannot exert a torque on AB. Thus the product alignment depends only on the magnitude of $\mathscr{R}$. In our reaction a large range of repulsive energy release is anticipated by comparison with reactive and photodissociative studies of F_2 [2]. This implies some corresponding spread in product vibration. Consequently the product alignment $\langle P_2(\hat{J}' \cdot \hat{k})\rangle$ must depend on product vibrational level v, consistent with data presented here. Thus, these measurements reflect the repulsive energy release as a function of product vibrational level. Preliminary studies indicate that simple impulsive models [17] are inadequate to explain our observations for $Ca + F_2$.

Acknowledgement

We thank J.A. Guest and K.H. Jackson for advice and assistance with the use of the photoelastic modulator. RNZ gratefully acknowledges support through the Shell Distinguished Chairs Program, funded by the Shell Companies Foundation, Inc. This work is supported by the National Science Foundation under NSF CHE 81-08823.

References

[1] R.D. Levine and R.B. Bernstein, Molecular reaction dynamics (Oxford Univ. Press, London, 1974).
[2] D.R. Herschbach, Faraday Discussions Chem. Soc. 55 (1973) 233; Advan. Chem. Phys. 10 (1966) 319.
[3] D.A. Case and D.R. Herschbach, Mol. Phys. 30 (1975) 1537; J. Chem. Phys. 64 (1976) 4212; 69 (1978) 150.
[4] M.R. Levy, Progr. Reaction Kinetics 10 (1979) 1.
[5] C.D. Jonah, R.N. Zare and Ch. Ottinger, J. Chem. Phys. 56 (1972) 263.
[6] M.G. Prisant, C.T. Rettner and R.N. Zare, J. Chem. Phys. 75 (1981) 2222.
[7] C.T. Rettner and J.P. Simons, Faraday Discussions Chem. Soc. 67 (1979) 329.
[8] R.J. Hennessy, Y. Ono and J.P. Simons, Mol. Phys. 43 (1981) 181.
[9] D.S. Hsu, N.D. Weinstein and D.R. Herschbach, Mol. Phys. 29 (1975) 257.
[10] M. Menzinger, Chem. Phys. 5 (1974) 350.
[11] F. Engelke, Chem. Phys. 44 (1979) 213; 39 (1979) 279.
[12] T. Kiang, R.C. Estler and R.N. Zare, J. Chem. Phys. 70 (1979) 5925.
[13] K.H. Jackson, Ph.D. Thesis, Stanford University, Stanford, California (1981).
[14] M. Dulick, P.F. Bernath and R.W. Field, Can. J. Phys. 58 (1980) 703.
[15] D.S.Y. Hsu and D.R. Herschbach, Faraday Discussion Chem. Soc. 55 (1973) 116.
[16] J.C. Polanyi, Accounts Chem. Res. 5 (1972) 161; Faraday Discussions Chem. Soc. 55 (1973) 389.
[17] J.C. Polanyi and J.L. Schreiber, in: Physical chemistry, an advanced treatise, Vol. 6A, eds. H. Eyring, D. Henderson and W. Jost (Academic Press, New York, 1974) p. 383.