Polanyi Memorial Lecture

By RICHARD N. ZARE

Department of Chemistry,
Stanford University, Stanford, California 94305, U.S.A.

Early workers in the field of chemical kinetics largely contented themselves with the measurement of reaction rates in terms of the concentrations of the interacting species. Michael Polanyi's experimental efforts were directed along the same lines. Polanyi's original idea was to form atomic or molecular beams of the reagents to be studied.[1] These beams were to be arranged so that they crossed. A measurement of the product flux would give the cross-section of the reaction from which the reaction rate could be calculated. However, experimental methods of the 1920s precluded the use of such techniques and instead Polanyi relied upon the ingenious use of diffusion flames.

Two reacting gases were admitted to opposite ends of a long glass tube. As they met, reaction was established. Some of the reactions produced visible chemiluminescence; others led to the formation of nonvolatile products that adhered to the walls of the tube. From the length of the reaction zone one could estimate how many scattering collisions occurred before reaction, based on a knowledge of diffusion theory and gas kinetic cross-sections. This method was used by Polanyi and coworkers to determine about one hundred reaction cross-sections, mostly for reactions of alkali atoms with halogen-containing molecules.[2] The cross-sections varied in size from a very tiny fraction of a gas kinetic collision cross-section to those much larger, so much larger that they might be figuratively compared to the size of a whale! These measurements were widely recognized to be of fundamental importance and were the precursors of extensive molecular beam studies of the very same systems.[3]

However, even more than his experimental work, Polanyi distinguished himself among kineticists by his inquiry into the relationship between the values of these reaction cross-sections and the structures and dynamics of the interacting species. Polanyi was one of the first to seek an explanation in terms of the forces between the reaction partners during a collisional encounter. For the generic bimolecular reaction $A + BC \rightarrow AB + C$, Polanyi adopted the theory of London (which we recognize today as the basis of the Born–Oppenheimer approximation) in which the nuclei of atoms move essentially according to the laws of classical mechanics under the potential given by quantum mechanics for some fixed ABC nuclear configuration. Together with H. Eyring, Polanyi constructed in 1931 a potential energy surface[4] to describe the reaction $H + H_2 \rightarrow H_2 + H$. Using transition state theory developed in his laboratory, calculations were made of the reaction rate with this potential energy surface. The conceptual innovation was born that an understanding of the main topological features of the potential energy surface is the first step toward a qualitative understanding of the reaction dynamics.

The potential energy surface was not purely theoretical; it employed empirical data in the form of the diatomic potentials of the reactants and products. Later

Sato[5] introduced parameters to control the form of the potential in the region where all three particles are strongly interacting. This so-called London–Eyring–Polanyi–Sato (LEPS) surface has become a touchstone against which all other potentials are compared.

So the seeds were sown for the study of reaction dynamics, a field that has produced a bounteous harvest of new insights into how chemical reactions occur. The bulk reaction rate is a macroscopic property of the reaction, representing an average over all reagent and product variables. It has been very difficult, therefore, to extract information about the dynamics from its measurement alone. To achieve a deeper insight, we must select the state of the reagent molecules and detect the state of the products. This measurement of " state-to-state kinetics " is becoming possible by the use of ever increasingly sophisticated spectroscopic and molecular beam techniques. We gather here to celebrate the 25th anniversary of the Discussion " Fast Reactions", held in Birmingham in 1954. Since that time the dream of using molecular beam techniques to study the microscopics of reaction dynamics has not only been realized but has become a mature field, providing us with some of the most detailed information on how reagents are transformed to products during a reactive encounter.[3] It is doubly fitting that we meet in Birmingham since this is the birthplace of the first reactive scattering beam experiments by Bull and Moon[6] on alkali metal atoms with carbon tetrachloride. Indeed, we will hear at this Discussion a revival of the Bull and Moon " swatter technique " to accelerate reagents by means of a spinning bat as well as discussion on the same reactive scattering system that Bull and Moon first investigated.

The fruit of our own labours also springs from the field Polanyi planted. I would like to share with you some recent results we have obtained on state-to-state reaction dynamics. The ideal chemical dynamics experiment in which angle, velocity and internal energy variables of both reactants and products are specified, can be approached best by a marriage between molecular spectroscopy and molecular beam techniques. One possible means of effecting this match is to use the method of laser induced fluorescence (LIF) for detection of the reaction products.[7] Here a tunable laser is scanned through an electronic absorption band of the product molecule.
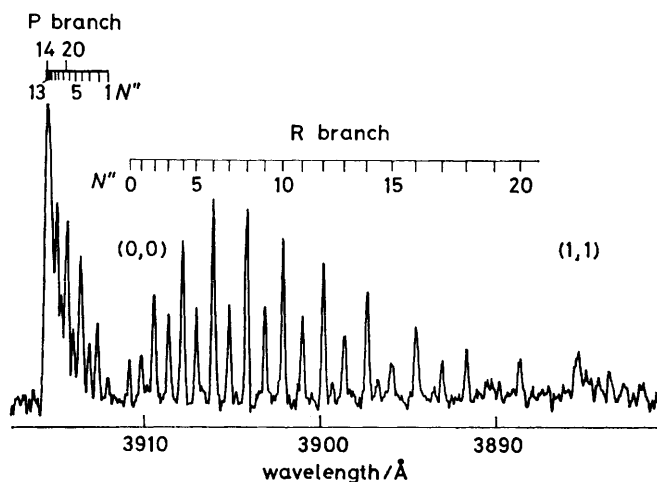

FIG. 1.—Excitation spectrum of N_2^+ X state ($B^2\Sigma_u^+ + X^2\Sigma_g^+$) produced by 100 eV electrons (100 μA) on N_2 (4×10^{-4} Torr).

When the laser wavelength coincides with a specific transition between internal (vibrational–rotational) energy levels, a fraction of those molecules in the (v'', J'') level of the ground state are pumped to the (v', J') level of the excited electronic state. Once there, the excited molecules can re-emit their energy (fluoresce) and this fluorescence may be detected very sensitively. By recording the total undispersed fluorescence intensity as a function of laser wavelength, one obtains an excitation spectrum that is very similar to the absorption spectrum of the molecular species under study.

Fig. 1 illustrates an excitation spectrum of N_2^+ taken in our laboratory by Allison and Kondow. The N_2^+ ions are formed by electron impact ionization of N_2 under collision-free conditions. The spectral resolution in fig. 1 is provided by the narrowness of the bandwidth of the tunable laser. If rotational line strengths (Hönl–London factors) and vibrational band strengths (Franck–Condon factors) are known or can be calculated, then relative populations of the internal levels of the ground state products may be derived from the excitation spectrum. For example, an analysis of fig. 1 shows that the rotational levels of the N_2^+ $v'' = 0$ state are populated in a manner well characterized by a temperature ($T_R = 323 \pm 5$ K).

While LIF can be exceedingly sensitive, it does not enjoy universal applicability. The products must have a strong electronic absorption band in the region covered by presently available tunable lasers, its spectroscopy and radiative properties must be known and the fluorescence quantum yield must be appreciable. These restrictions usually limit LIF usefulness to diatomic and some selected small polyatomic molecules, but when the LIF detection method can be applied, the information obtained often is remarkably rich.
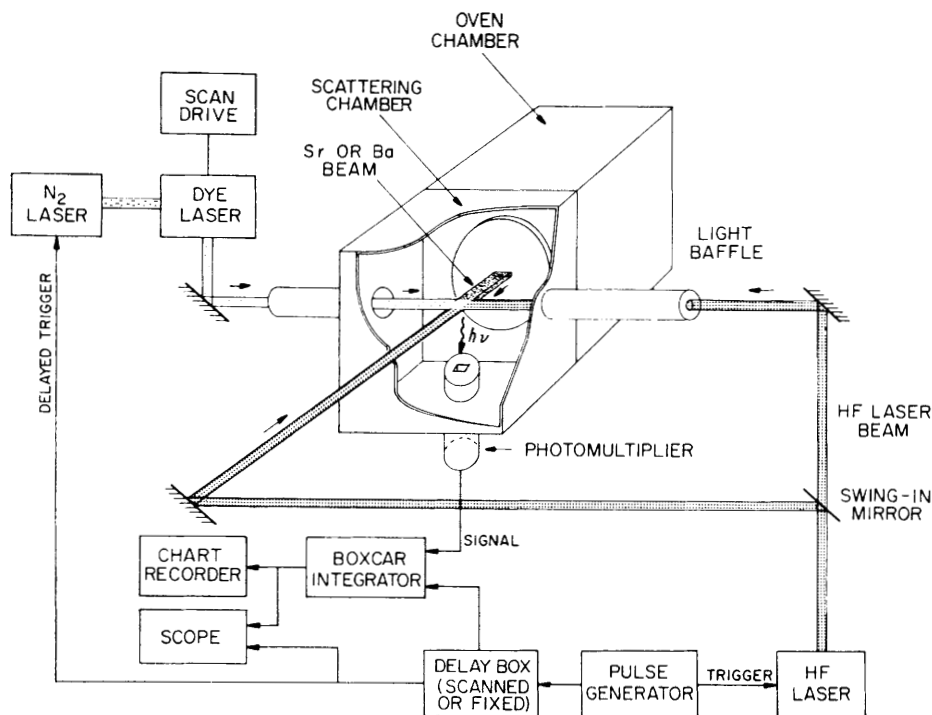

FIG. 2.—Cutaway drawing of the beam-gas experimental setup. A swing-in mirror permits excitation of the HF molecules in the scattering chamber by two different light paths, one antiparallel, the other perpendicular to the probe laser beam.

For some time we have been examining the reactions

$$M + HF \rightarrow MF + H \tag{1}$$

where M is an alkaline earth atom. This is an interesting family of reactions because
it contains both exothermic and endothermic members and it typifies a transformation
from a covalently-bound reagent to an ionically-bound product. The alkaline earth
monofluorides have several strongly allowed electronic transitions in the visible,
making their detection by LIF quite straightforward. The HF reagent can be con-
trolled using a pulsed HF laser tuned to a selected vibrational–rotational level or
using a seeded nozzle beam to enhance translational energy in a known manner.
Fig. 2 shows a schematic view of the apparatus placed in a beam-gas configuration.
A beam of alkaline earth atoms traverses a scattering chamber filled with HF gas at
sufficiently low pressures (1×10^{-4} Torr) that collisional relaxation of the products
is negligible. The HF laser beam can be directed either along the metal beam or at
right angles to it.

The exothermic reaction

$$Ba + HF \rightarrow BaF + H; \quad \Delta H_0^0 = -18 \text{ kJ mol}^{-1} \tag{2}$$
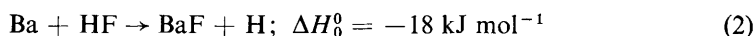
occurs with a large cross-section without HF vibrational excitation. By subtracting
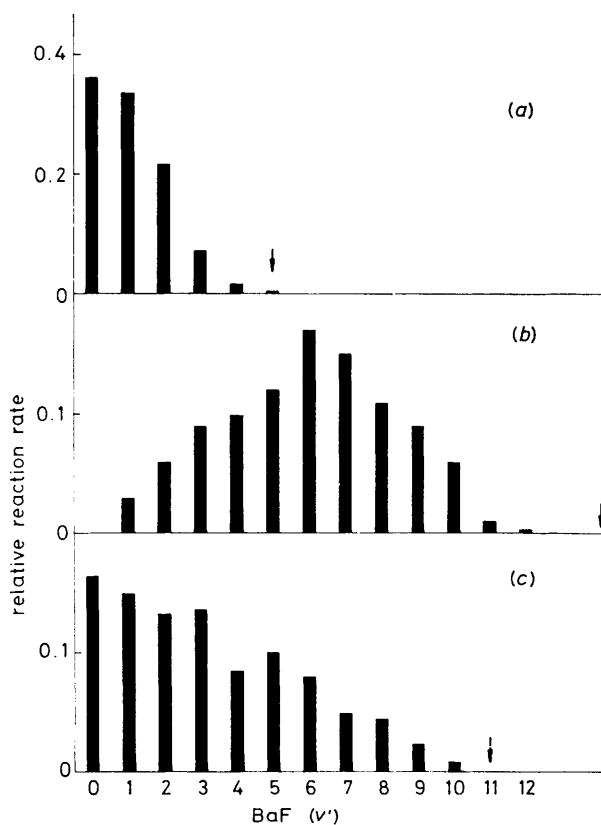

FIG. 3.—Vibrational population distribution of the BaF product formed in the reaction Ba + HF
for different HF reagent translational and internal energies. The arrows indicate the reaction exo-
thermicity limits. (a) $v(HF) = 0$, $T = 1.6$ kcal mol^{-1}; (b) $v(HF) = 1$, $T = 1.6$ kcal mol^{-1}; (c)
$v(HF) = 0$, $T = 10.2$ kcal mol^{-1}.

with the help of a difference circuit the BaF fluorescence intensity when the HF laser was off from the intensity when the HF laser was on, Pruett and Zare[8] obtained the BaF excitation spectrum resulting from reaction of Ba with HF($v = 1$). Fig. 3 presents the relative vibrational populations of the products. Of the 46 kJ mol^{-1} represented by the reagent HF vibrational excitation, some 57% appears as product vibration.

In our laboratory, Perry and Gupta seeded an HF beam with He or H$_2$ and crossed it with an effusive Ba source (beam–beam configuration; see fig. 4). Fig. 5 compares
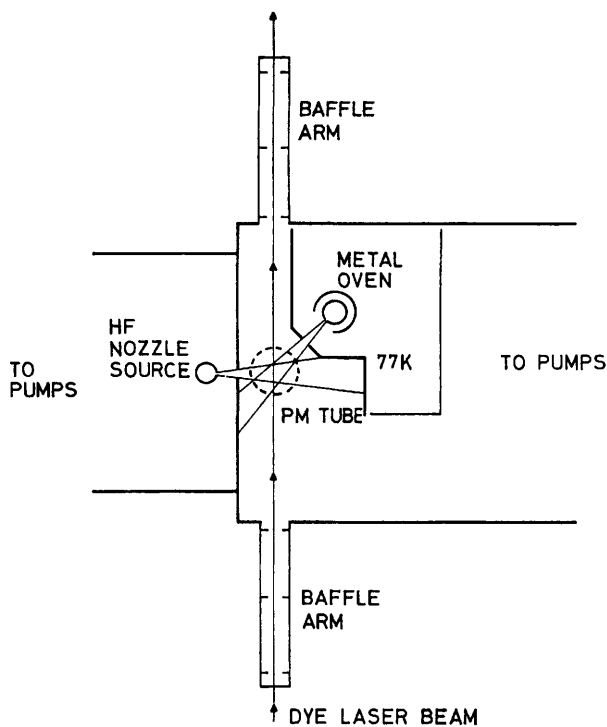

FIG. 4.—Crossed beam set-up for studying the effect of HF reagent translational energy on product yield and product internal state distribution.

the BaF excitation spectra obtained at high and low collision energies. At 43 kJ mol^{-1} in collision energy, R$_1$ bandheads appear which are not observed at the lower collision energy. The presence of these R$_1$ bandheads signifies high product rotational excitation. At high collision energy, additional vibrational levels of BaF are populated but the product vibrational distribution continues to peak at $v'' = 0$ (see fig. 3). This contrasts with the effect of reagent vibration which shifts the peak of the distribution to $v'' = 6$. The added 36 kJ mol^{-1} in collision energy is transformed into 51% translation, 28% rotation and 21% vibration of the product.

Yet another important conceptual advance in this field is due in part to Michael Polanyi, namely, his son John. From a study of classical trajectories on LEPS surfaces J. C. Polanyi and coworkers[9] have arrived at the general rule that additional reagent vibration, ΔV, appears as product vibration, $\Delta V'$, while additional collisional energy, ΔT, is transformed into product translational and rotational energy, $\Delta T'$
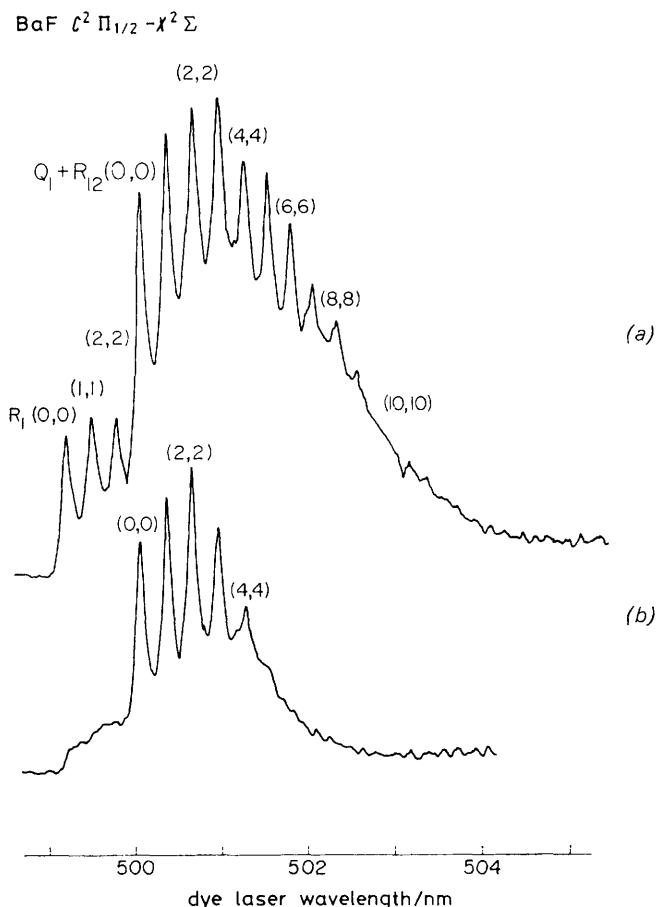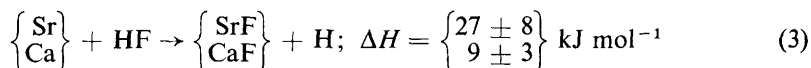
FIG. 5.—Excitation spectra of the BaF product formed by the reaction Ba + HF → BaF + H at different relative initial kinetic energies. (a) $\langle T \rangle$ = 10.2 kcal mol^{-1}; (b) $\langle T \rangle$ = 3.7 kcal mol^{-1}.

+ $\Delta R'$. Our findings for Ba + HF are in qualitative but not quantitative agreement with these generalizations.

The above studies have been extended to the endothermic reactions

$$\begin{Bmatrix} Sr \\ Ca \end{Bmatrix} + HF \rightarrow \begin{Bmatrix} SrF \\ CaF \end{Bmatrix} + H; \quad \Delta H = \begin{Bmatrix} 27 \pm 8 \\ 9 \pm 3 \end{Bmatrix} \text{ kJ mol}^{-1} \qquad (3)$$

which do not proceed readily under thermal conditions. However, Karny and Zare[10] have found that the rates of these reactions increase by at least four orders of magnitude when the HF is excited into its first vibrational state. Fig. 6 shows some sample excitation spectra.

This reaction system offers the opportunity to compare the effectiveness of reagent vibration and translation in promoting an endothermic reaction at the same total energy. To date there is only one direct experimental comparison for an endothermic reaction. Brooks and coworkers[11] found for the marginally endothermic reaction

$$K + HCl \rightarrow KCl + H; \quad \Delta H = +6 \text{ kJ mol}^{-1} \qquad (4)$$
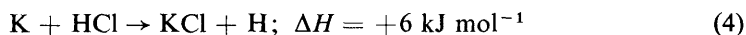
that HCl(v = 1) has a reaction cross-section about ten times that of HCl(v = 0) with the same amount of translational energy.

SrF $A^2\Pi_{3/2} - X^2\Sigma^+$
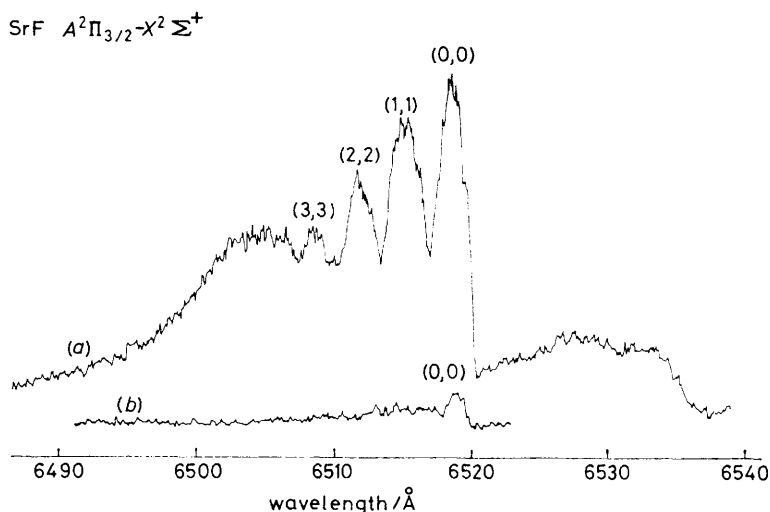

FIG. 6.—Excitation spectra of the SrF product resulting from the reactions (*a*) Sr + HF($v = 1$) and (*b*) Sr + HF($v = 0$).

To carry out the corresponding comparison for Sr + HF, the Ba + HF reaction is used as an internal reference standard.   A mixed alkaline earth atom beam is prepared by combining equimolar quantities of barium and strontium.   This beam is crossed with the seeded HF beam and the BaF to SrF product yields are compared. The same comparison is also made in the beam–gas configuration to determine the intensity ratio I[Sr + HF($v = 1$)] to I[Ba + HF($v = 0$)].   With the assumption that the cross section for the exothermic reaction Ba + HF does not change with collision energy, we find the preliminary value of the cross-section ratio at the same total energy:

$$\frac{\sigma[\text{Sr} + \text{HF}(v = 1, E_\text{T} = 7 \text{ kJ mol}^{-1})]}{\sigma[\text{Sr} + \text{HF}(v = 0, E_\text{T} = 54 \text{ kJ mol}^{-1})]} \approx 15. \tag{5}$$

Eqn (5) should be no more uncertain than a factor of three.
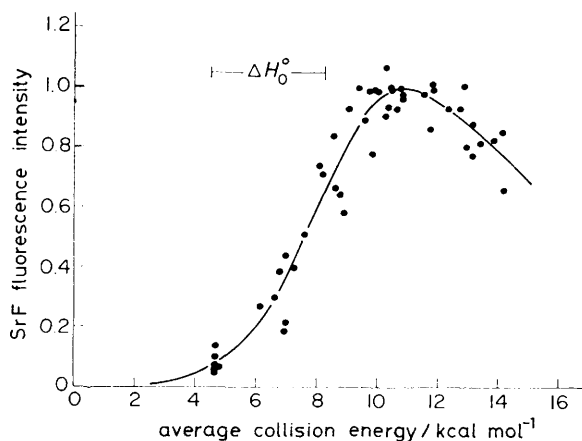

FIG. 7.—Fluorescence intensity of SrF product as a function of relative initial kinetic energy.   The quantity, ΔH_0^0, reflects the present uncertainty in the heat of reaction.   A deconvolution of this data to correct for the spread in collision energy and the variation of beam intensity with seeding ratio would accentuate both the rise and fall-off.

This result supports the generalization that vibration is more effective than translation in promoting an endothermic reaction.[12]   However, since Sr + HF is much more endothermic than K + HCl, one might have expected a larger ratio even though the potential energy surfaces may differ.   Using the principle of microscopic reversibility, J. C. Polanyi, R. B. Bernstein and coworkers[13] have obtained the above ratio for several endothermic reactions from studies of the reverse exothermic reactions. They find that at constant total energy, vibrational excitation of the reagent is typically two to three orders of magnitude more efficacious that translational energy in promoting endothermic reaction.   Thus the Sr + HF reaction contrasts with these reactions in that translational energy is qualitatively more effective.

Could it be that the Sr + HF reaction proceeds through a complex?   Because of the divalent character of the alkaline earth atoms, the H—M—F configuration will lead to a well in the potential energy surface.   This may cause reagent translational energy to be coupled more effectively to motion along the reaction coordinate.   This would account for the relatively steep falloff in SrF product yield with relative initial translational energy above 50 kJ mol^{-1} (see fig. 7).   This type of complex may also be formed in the reaction Ba + HF which would help to explain the quantitative deviations from J. C. Polanyi's generalizations, $\Delta V \rightarrow \Delta V'$ and $\Delta T \rightarrow \Delta T' + \Delta R'$.
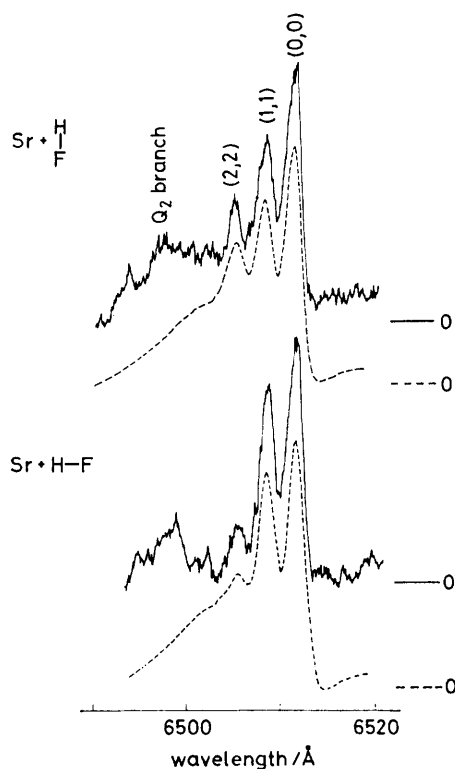

FIG. 8.—Excitation spectra for Sr + HF($v = 1$, $J = 1$) with the HF molecule preferentially aligned perpendicular to the Sr atom approach direction (upper trace) or parallel to the Sr atom approach direction (lower trace).   The dashed curves are computer simulations assuming a rotational temperature of 800 K for all vibrational levels.   The baselines are indicated for comparison purposes.   For the $J = 1$ case, the HF molecules are prepared with a $3 + \cos^2\theta$ distribution, where θ is the angle between the electric vector of the light beam and the internuclear axis of the molecule.

Yet subtler questions about the dynamics of the Sr + HF reaction can be posed and resolved experimentally with the help of laser preparation of the reagent. For example, Karny, Estler and Zare[14] have demonstrated the importance of reagent rotation and orientation. The latter deserves special mention as it is a step from scalar to vector measurements characterizing the reactive collision.[15] The output of the HF laser is linearly polarized and the plane of polarization may be selected by means of a Fresnel rhomb (fig. 2). Thus the HF($v = 1$) reagent molecules are prepared so that the Sr collision partner preferentially approaches the HF internuclear axis either in the collinear or broadside configuration, on the average. Fig. 8 shows the resultant excitation spectra for these two " average " collision geometries. It is clearly seen that broadside attack favours the population of higher vibrational levels in the SrF product. If one believes that attractive energy release is correlated with product excitation,[16] then this result supports recent theoretical calculations[17,18] indicating that the minimum energy path of the reactions of alkali and alkaline earth atoms with hydrogen fluoride proceeds through a highly bent configuration.

There are many advantages to the preparation of oriented reagents by optical pumping: the degree of selection is high; the degree of selection is well defined; and the optical pumping process permits state selection as well as orientation. Clearly the study of reagent orientation upon chemical reactivity and product state distribution is still a relatively uncultivated spot in Michael Polanyi's garden on which many flowers may bloom.[19] It has the promise of allowing chemists to explore and control the stereodynamics of reaction pathways.

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