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COMMUNICATIONS

Observation of a steric effect in the reaction of Xe^* with photodissociation polarized IBr^a

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Molecular collision processes have been studied as a function of many different parameters. However, few studies have been done on the effect of approach geometry, since it is one of the most difficult parameters to control. Beams of polar molecules have been oriented using hexapolar fields.¹ Zare and co-workers² have shown that optical alignment of reactive species with suitable lasers can be used to study orientation effects in chemical reactions. This has led to experiments with polarized atoms and molecules in excited states,² and polarized ions.³ It has been shown that polarization of ground state diatomic molecules can also be obtained by using photodissociation to selectively remove most of the M state distribution.⁴ In this communication we report the first use of photodissociation polarization to study a reaction cross section as a function of ground-state molecular orientation.

Molecules can be polarized by optical excitation because the absorption of dipole radiation is M -state dependent.⁵ Classically, the absorption probability is proportional to $\cos^2 \eta$, where η is the angle between the light vector $\vec{\epsilon}$ and the transition dipole moment $\vec{\mu}$. The latter is fixed with respect to the molecular structure. For the present IBr transitions $\vec{\mu}$ is parallel to the internuclear axis, so the absorption probability goes to zero for molecules rotating in a plane perpendicular to the light vector (η always equals $\pi/2$ and $M = \pm J$). Upon excitation to a repulsive state, those molecules that absorb a photon dissociate, leaving the remaining ground-state molecules rotationally polarized. A high degree of polarization is obtained when the transition is close to saturation. In the case of a parallel transition only molecules rotating perpendicularly to the light vector would remain in the saturation limit.

We have studied the reaction of polarized IBr with $\text{Xe}(^3P_{0,2})$, producing the XeBr^* and XeI^* excimers. A Xe nozzle beam was passed through a Penning discharge to produce metastables, and then crossed at right angles with an effusive IBr beam. Chemiluminescence from the excimers was observed with a photomultiplier perpendicular to the IBr beam and at 60° with respect to the Xe^* beam. The IBr was photodissociated by light from a frequency doubled, pulsed Nd:YAG laser at 532 nm. The laser beam was perpendicular to the Xe^* and

IBr beams, and intersected the IBr beam partly in and partly just before the interaction region. The excimer emission intensity is shown as a function of time following the laser pulse in Fig. 1. The emission decreases as the dip in the IBr beam moves into the interaction region, and then increases back to the dc level as the dip exits the interaction region. Experimental tests showed that this effect was due to interaction of the laser beam with the IBr beam, and not with the Xe^* beam. The chemiluminescence intensity I due to the reaction of polarized IBr was determined by averaging the first ten time channels of plots such as Fig. 1, and the dc intensity I_0 was determined from the average of ten time channels starting after $60 \mu\text{s}$. The percent residual chemiluminescent signal ($100I/I_0$) from the reaction of polarized IBr was then measured as a function of laser polarization angle. The light vector was rotated with a halfwave plate and measurements were made at 30° intervals, giving the results shown in Fig. 2. It is found that the reaction cross section is largest for $\theta_{\text{cm}} = 90^\circ$ and smallest for $\theta_{\text{cm}} = 0^\circ$, where θ_{cm} is the angle between the $\text{Xe}^* + \text{IBr}$ relative velocity vector \vec{v} and the light vector $\vec{\epsilon}$. The IBr molecules are polarized with the most probable plane of rotation perpendicular to $\vec{\epsilon}$. Therefore, the reaction cross section is largest when Xe^* approaches parallel to the plane of rotation of the IBr , and smallest when Xe^* approaches perpendicular to the plane of rotation.

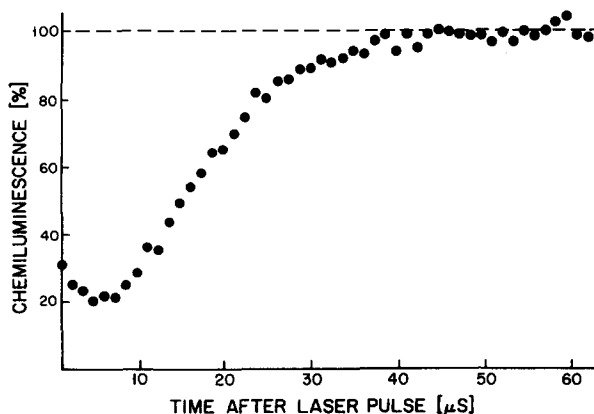


FIG. 1. Chemiluminescence signal as a function of time after the laser pulse. Broken line indicates dc signal with laser off.

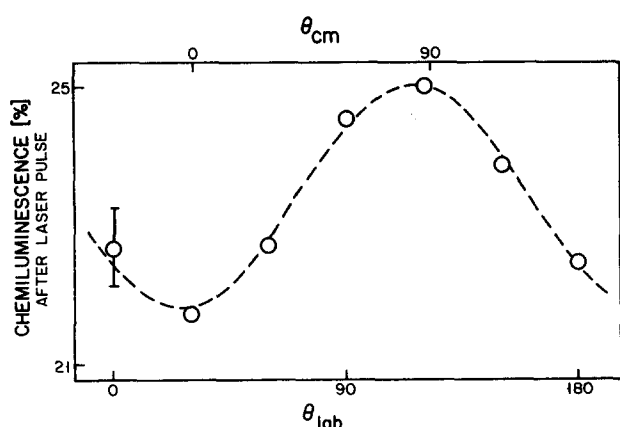


FIG. 2. Chemiluminescence after the laser pulse as a function of the angle between the light vector and the atomic beam θ_{lab} . The angle between the light vector and the most probable $\text{Xe}^* + \text{IBr}$ relative velocity vector θ_{cm} is indicated on the top scale.

The above conclusion is based on models which show that the dependence of the chemiluminescence intensity on θ_{cm} is a cross-section effect rather than a result of anisotropic emission from polarized excimers. If the polarized angular momentum of the reactant IBr was transformed to polarized angular momentum of the product excimers, the resulting excimer intensity would depend on θ_{lab} . However, the maximum emission would be at $\theta_{lab} = 0^\circ$ and the minimum emission at $\theta_{lab} = 90^\circ$, in contradiction to the experimental results. It should also be noted that excimer formation involves harpoon-type reactions in which the average orbital angular momentum is much larger than the diatomic rotational angular momentum.⁶ As a result, the product

M -state distribution is not expected to be very sensitive to the reactant M -state distribution.⁷

Harpoon reactions involve curve crossings, and the coupling matrix elements between the curves can be strongly orientation dependent.⁸ This can lead to strong anisotropies in the potentials near crossings, resulting in orientation dependent reaction cross sections. This is thought to be responsible for the effect seen in Fig. 2. A detailed model explaining these results will be discussed in a subsequent paper.

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Semiclassical prediction of resonance energies in three-dimensional reactive collisions^{a)}

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In this communication, a novel and practical semiclassical approach to resonances in three-dimensional chemical reactions is described and applied to the lowest-energy resonances in the $\text{H} + \text{H}_2$ and $\text{F} + \text{H}_2$ reactions. For the former, the shift in the resonance energy with increasing dimensionality is emphasized, while for the latter, the angular momentum variation of the resonance energy is studied. In both cases, good agreement with results from (difficult and expensive) quantum calculations is found.

The first predictions of resonances appeared over a decade ago in quantum collinear reactive scattering calculations.¹ The picture that emerges from quantal

analysis is trapping in vibrationally adiabatic wells in the interaction region of the potential surface.² The semiclassical analog of these resonances involves long-lived "trapped" trajectories.^{3,4} For collinear reactions, the quantal resonance energies are predicted extremely well by resonant periodic orbits (RPOs) obeying integer action quantization conditions.⁴ For the collinear $\text{F} + \text{H}_2$ reaction,⁵ the lowest resonance is found quantally⁶ at $E_r = 0.284$ eV, while an RPO with an action of $4h$ is found at $E_r = 0.282$ eV. Several RPOs for the FH_2 system are illustrated in Fig. 5 of Ref. 4. Note that these trajectories bounce repeatedly between the H_2 valley and the FH valley.