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Huge steric effect in the reaction Li$+$HF($v=1, j=1$)$\rightarrow$LiF$+$H

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The influence of the collision geometry on bimolecular reactions is experimentally well established[1–5] but owing to the lack of precise *ab initio* potential energy surfaces (PESs) for the systems investigated so far, the experimental data could not be compared with theoretical predictions. For Li + HF, however, a reliable *ab initio* PES exists.[6] In the present letter we report steric effects observed in a crossed beam study on the title reaction and the results of a trajectory calculation based on this PES.

The experimental configuration, including the infrared radiation pumping technique which we employ to prepare the collision geometry, has been described in more detail elsewhere.[4,7] Briefly, the infrared radiation of a color center laser was irradiated perpendicularly onto an HF nozzle beam. The laser was tuned to the $R_1(0)$ transition to pump a fraction of the molecules into the $v=1$, $j=1$, $m=0$ state. This state exhibits a marked alignment of the molecular axis but—without taking precautions—the optically prepared polarization is destroyed within a few microseconds by nuclear spin–rotation coupling.[8] To avoid this we generate—deviating from Refs. 4 and 7—an electric field which extends from the excitation zone to the reaction volume. The field dependence of the measured steric effects indicates that complete decoupling is obtained already at a field strength>3 kV/cm. The polarization vector of the infrared radiation was set parallel to the field ($\mathbf{E}_s$) and thus the selection rule $\Delta m=0$ applies with respect to $\mathbf{E}_s$ as quantization axis. The field at the intersection of the reagent beams (guiding field, $\mathbf{E}_g$) can be chosen to be either parallel or perpendicular to the mean relative velocity of the reagents, $\mathbf{V}$. The field strength (≈ 10 kV/cm) and the shape of the electrodes were chosen such that a molecule which moves downstream from the excitation zone to the reaction volume experiences a field whose direction changes sufficiently slowly so that the prepared state can adiabatically follow the rotating quantization axis.

The density function $\widetilde{A}$ describing the probability for finding the molecular axis pointing into a certain direction is given by the square modulus of the prepared rotor eigenfunction $Y_{1,0}$, where $m=0$ refers to the quantization axis $\mathbf{E}_g$. With respect to $\mathbf{V}$ as quantization axis two distributions result which are given by

$$\widetilde{A}_{\|}=\frac{3}{4\pi}\cdot\cos^2\gamma_a, \tag{1}$$

$$\widetilde{A}_{\perp}=\frac{3}{4\pi}\cdot\sin^2\gamma_a\cdot\cos^2\phi_a \tag{2}$$

for $\mathbf{E}_g\|\mathbf{V}$ and $\mathbf{E}_g\perp\mathbf{V}$, respectively; γ_a denotes the angle of attack between $\mathbf{V}$ and the molecular axis and ϕ_a is the azimuthal angle of the latter with respect to an axis perpendicular to the scattering plane. For $\mathbf{E}_g\|\mathbf{V}$ the approaching atoms attack preferentially the ends of the molecules while for the second field direction side-on attacks prevail.

The experiments were performed at a mean relative translational energy of $E_{\mathrm{tr}}=0.4$ eV with the detector set to a laboratory deflection angle of $\Theta=64°$ in the plane of the two reagent beams. The results are displayed in Fig. 1, together with the nominal kinematic diagram. Plotted is the flux of products for $\mathbf{E}_g\|\mathbf{V}$ and $\perp\mathbf{V}$ as a function of time in chronological order. The acquisition time per point was 5 min; the average over all points is indicated by the straight solid line. The effect of the field direction on the signal is very drastic; the product flux rises by a factor of 2.2 if the field is rotated from $\perp\mathbf{V}$ to $\|\mathbf{V}$. In other words, end-on attacks send more products into the detector than side-on attacks.

To rationalize this huge steric effect we performed a quasiclassical trajectory study. As PES we used Carter and Murrell's[9] analytic expression based on the *ab initio* points of Chen and Schaefer.[6] The function had to be modified somewhat to obtain a smooth asymptotic behavior.[10,11] To simulate the prepared axis distributions we set the initial angular momentum of HF to zero and generate $\cos\gamma_a$ and ϕ_a such that these quantities are distributed according to Eq. (1) or (2). The distribution $\widetilde{A}_{\perp}$ destroys the familiar cylindrical symmetry around $\mathbf{V}$ of the scattering problem. Thus, deviating from most trajectory calculations, both the polar and azimuthal scattering angles in the center-of-mass (c.m.) frame, ϑ and ϕ, of the molecular products were determined and boxed into equidistant $\Delta\vartheta$ intervals (18°) *and* $\Delta\phi$ intervals (22.5°).

We have calculated 5000 trajectories for each direction of $\mathbf{E}_g$ at a relative translational energy of 0.4 eV. Figure 2 shows the differential cross section for in plane scattering (all trajectories with $67.5°\leqslant\phi\leqslant112.5°$ are accepted) in the c.m. frame. Both histograms exhibit a prominent peak but the position and height of the maxima differ drastically. The integral reaction cross sections are equal within the statistical error and amount to (7.8 ± 0.2 Å^2). As a more detailed analysis shows, the differences are mainly caused by the propensity of the two products to separate in opposite directions *along the molecular axis.* As for $\mathbf{E}_g\perp\mathbf{V}$ the axes stand preferentially perpendicular to the scattering plane, a substantial fraction of products is scattered above or below the plane ($\phi=90°$), and is thus lost for the in plane flux. In case $\mathbf{E}_g\|\mathbf{V}$ the axes are symmetrically distributed around $\mathbf{V}$ and thus the preference for out of plane scattering vanishes. Consequently, more products appear in plane and the peak of the cross section becomes higher.

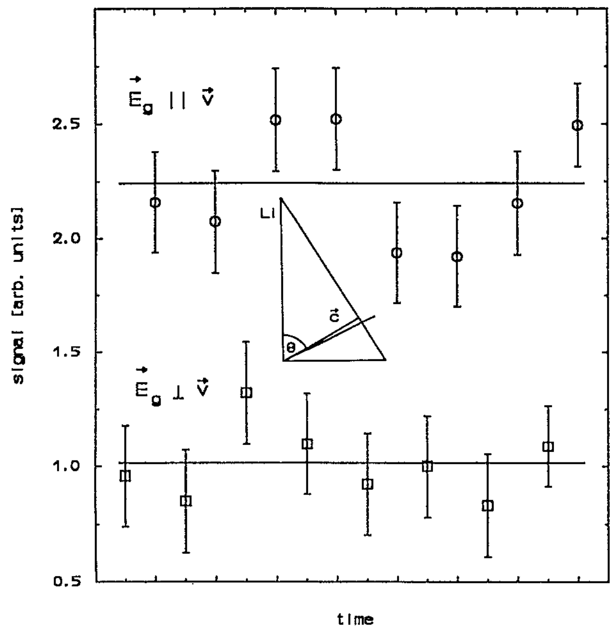

FIG. 1. Temporal dependence of signal measured for the indicated field directions (E_{tr} = 0.4 eV, $\Theta = 64°$). The insert illustrates the nominal kinematics.

The preferred backward scattering for $\mathbf{E}_g \| \mathbf{V}$ reflects the asymmetric reactivity of the two ends of HF. Only attacks on the F-end form products. After initiation of the reaction the H atom is ejected along the HF axis into the forward direction of the c.m. frame and the detected LiF into the backward direction.

Figure 3 exhibits the steric effect $S(\vartheta)$ defined here by the ratio of the difference and sum of the histograms (Fig. 2) as a function of ϑ. The substantial difference in position and height of the maxima leads to an oscillatory behavior where $S(\vartheta)$ ranges from $\approx +0.6$ for backward scattering to ≈ -0.6 for forward scattering. From the data of Fig. 1 we deduce an experimental steric effect of $S_{\rm exp} = 0.38$ which represents roughly $S(\vartheta)$ averaged over the range $105° \leqslant \vartheta \leqslant 125°$. For comparison $S_{\rm exp}$ is given in Fig. 3 together with the experimental error; the covered ϑ range is indicated by the horizontal bar. Theory predicts correctly the sign of the observed steric effect and overestimates its magnitude by 40%. Measurements concerning the angular distribution of the steric effect are in progress.

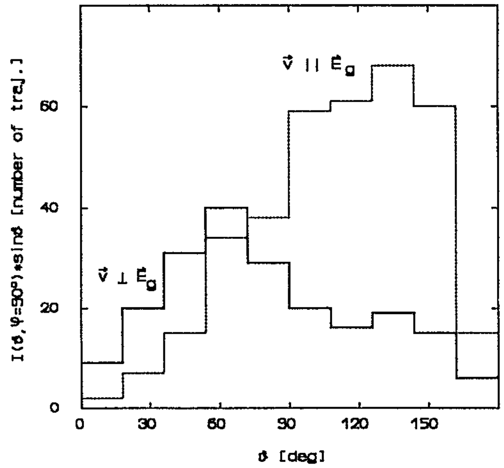

FIG. 2. Differential in plane reaction cross section as a function of ϑ calculated for the indicated field directions (E_{tr} = 0.4 eV).

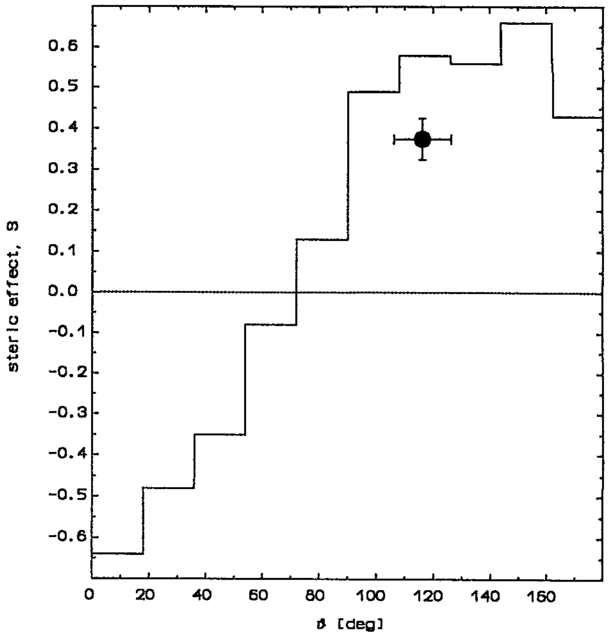

FIG. 3. Angular dependence of the steric effect $S = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ deduced from Fig. 2. The full circle represents the experimental result.

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[1] P. R. Brooks, Science **193**, 11 (1976).
[2] R. B. Bernstein, D. R. Herschbach, and R. D. Levine, J. Phys. Chem. **91**, 5365 (1987).
[3] S. Stolte, *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University, New York, 1988), Vol. 1, Chap. 25.
[4] M. Hoffmeister, R. Schleysing, and H. J. Loesch, J. Phys. Chem. **91**, 5441 (1987).
[5] H. J. Loesch and A. Remscheid, J. Chem. Phys. **93**, 4779 (1990).
[6] M. M. L. Chen and H. F. Schaefer III, J. Chem. Phys. **72**, 4376 (1980).
[7] M. Hoffmeister, R. Schleysing, F. Stienkemeier, and H. J. Loesch, J. Chem. Phys. **90**, 3528 (1989).
[8] R. Altkorn, R. N. Zare, and C. H. Greene, Mol. Phys. **55**, 1 (1985).
[9] S. Carter and J. N. Murrell, Mol. Phys. **41**, 567 (1980).
[10] H. J. Loesch, Chem. Phys. **104**, 213 (1985).
[11] H. Zerhau-Dreihöfer, Diplomarbeit, Universität Bielefeld, Germany, 1986.