Photofragment Angular Distributions

The use of a linearly polarized laser to photodissociate 2-bromoethanol allows us to study the angular distribution of the C-Br bond fission photofragments. [S1-S4] Figures S1, S2, and S3 show the recoil angular distributions for $Br(^2P_{1/2})$, $Br(^2P_{3/2})$, and C_2H_4OH, respectively. The $Br(^2P_{1/2})$ image in Figure 1 of the manuscript has highest intensity along the laser polarization axis, which is consistent with a transition dipole moment that is parallel with the breaking C-Br bond. The following expression fits the $Br(P_{1/2})$ angular distribution in Figure S1:

$$I(\theta) \propto 1 + \beta P_2(\cos\theta) \qquad \text{(S1)}$$

where θ is the angle between the recoiling fragment's velocity and the electric vector of the photolysis laser, $I(\theta)$ is the integrated ion signal over a certain speed range at angle θ, $P_2(\cos\theta)$ is the second-order Legendre polynomial, and β is the anisotropy parameter. (β can range from -1 to +2, where -1 corresponds to axial recoil following a perpendicular transition and +2 corresponds to axial recoil following a parallel transition upon photoexcitation of the parent molecule.) The signal appearing in the $Br(^2P_{1/2})$ image in the range from 260-312 pixels from the center of the image corresponds to a recoil kinetic energy range of 28-40 kcal/mol, or 1032-1240 m/s (for vertically recoiling fragments), and is characterized by an anisotropy parameter of β = 0.55. The signal appearing 260-320 pixels from the center of the image corresponds to a recoil kinetic energy range of 28-42 kcal/mol, or 1032-1270 m/s (for vertically recoiling fragments), is characterized by an anisotropy parameter of β = 0.58. The anisotropy shows a marked velocity dependence with the highest velocity $Br(^2P_{1/2})$ signal approaching a completely parallel transition.

The highest intensity signal in the $Br(^2P_{3/2})$ image is perpendicular to the laser polarization axis, indicating that the transition dipole moment for this photodissociation process is perpendicular to the breaking C-Br bond. However, the angular distribution for ground-state bromine cannot fit by Equation S1. The $Br(^2P_{3/2})$ atoms have a spin-orbit angular momentum quantum number (J) larger than ½ and may have an aligned m_J distribution, which can influence the efficiency of the linearly polarized REMPI process. Thus, the following expression fits the detected $Br(P_{3/2})$ angular distribution shown in Figure S2:

$$I(\theta) \propto 1 + \beta_2 P_2(\cos\theta) + \beta_4 P_4(\cos\theta) \qquad \text{(S2)}$$

Note that the β_2 in Equation S2 is not equal to the spatial anisotropy parameter β in Equation S1. The signal appearing in the range of 260-312 pixels from the center of the $Br(^2P_{3/2})$ image (which again corresponds to vertically recoiling fragments with E_T = 28-40 kcal/mol or 1032-1240 m/s) corresponds to β_2 = -0.24 and β_4 = -0.05. The signal appearing in the range 260-340 pixels from the center of the image (28-47 kcal/mol 1032-1350 m/s) corresponds to β_2 = -0.20 and β_4 = -0.05. The anisotropy parameter becomes more isotropic at higher recoil velocities. If we neglect the small β_4 value and assume that β_2 approximates the photodissociation anisotropy in Equation S1 for the $Br(^2P_{3/2})$ signal, we can calculate the average anisotropy for all of the C-Br bond fission events. Weighting β = 0.58 and β= -0.20 by the spin-orbit branching ratio gives an average anisotropy of β = -0.04. This is consistent with the isotropic distribution that Y.T. Lee and co-workers observed from their detection of all Br atoms. Y. T. Lee and co-workers

speculated that the isotropic distribution for the Br atoms was the result of a large geometrical rearrangement of 2-bromoethanol during photodissociation due to the intramolecular OH-Br hydrogen bonding of the Gg conformer, but here we resolve the spin orbit states and see that the overall isotropic distribution contains contributions with parallel character from the Br($^2P_{1/2}$) and perpendicular character from the Br($^2P_{3/2}$) photofragments.

Integrating the C_2H_4OH signal over the range of 250-325 pixels from the center of the image (1740-2265 m/s) and fitting it to Equation S1, we find the anisotropy parameter for stable C_2H_4OH radicals to be -0.15, as shown in Figure S3. We were unable to subtract from these data the background contribution due to laser light hitting the ion optics. We can also use our model from Section D of the manuscript and the measured anisotropies for the Br($^2P_{3/2}$) + C_2H_4OH and Br($^2P_{1/2}$) + C_2H_4OH channels to predict the anisotropy of the energetically stable C_2H_4OH radicals. The model producing the prediction shown in Figure 8(d) of the manuscript, which included zero-point and thermal vibrational motion along the 217.8 cm^{-1} mode and the range of internal energies of the Tt conformer, predicts that 63.7% of the energetically stable C_2H_4OH radicals are momentum matched to Br($^2P_{3/2}$) while 36.3% are momentum matched to Br($^2P_{1/2}$). Weighting the measured anisotropies for each Br spin-orbit state by this predicted abundance gives an anisotropy of $\beta = 0.08$ for the predicted stable C_2H_4OH radicals. The model used for the prediction in Figure 9 predicts 31.2% of the energetically stable C_2H_4OH radicals are momentum matched to Br($^2P_{3/2}$) while 68.8% are momentum matched to Br($^2P_{1/2}$); this predicts an anisotropy of β=0.04 for the predicted stable C_2H_4OH radicals. While these predicted anisotropies are not in agreement with our measured anisotropy, the excited state isomerization of 2-bromoethanol from gauche to trans about the C-C bond can substantially alter the angular distribution of the resulting photofragments.

(S1) Rakitzis, T. P.; Zare, R. N. *J. Chem. Phys.* **1999**, *110*, 3341.
(S2) Rakitzis, T. P.; Kandel, S. A.; Alexander, A. J.; Kim, Z. H.; Zare, R. N. *J. Chem. Phys.* **1999**, *110*, 3351.
(S3) Samartzis, P. C.; Bakker, B. L. G.; Rakitzis, P.; Parker, D. H.; Kitsopoulos, T. N. *J. Chem. Phys.* **1999**, *110*, 5201.
(S4) Bass, M. J.; Brouard, M.; Clark, A. P.; Vallance, C.; Martinez, Haya. *Phys. Chem. Chem. Phys.* **2003**, *5*, 856.

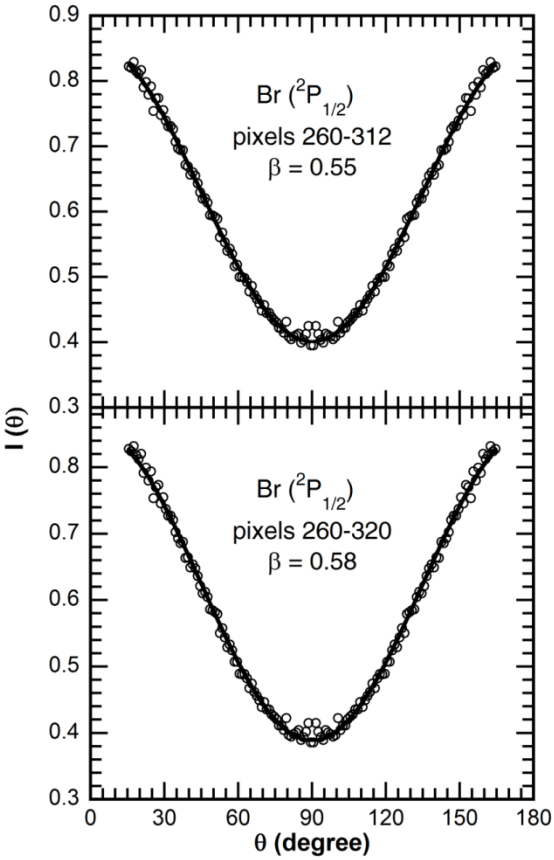

Figure S1

Angular distribution for Br($^2P_{1/2}$) detected 260-312 (top) and 260 -320 pixels (bottom) from the center of the ion image shown in Figure 1 of the manuscript.

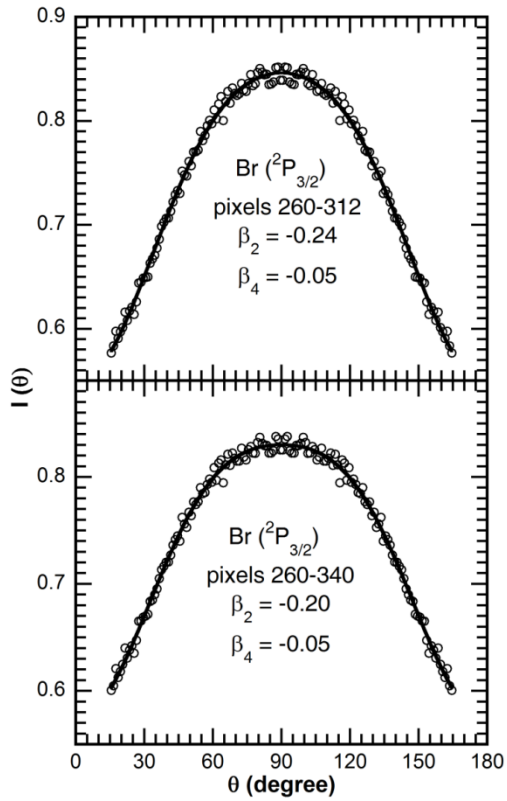

Figure S2

Angular distribution for Br($^2P_{3/2}$) detected 260-312 (top) and 260 -340 pixels (bottom) from the center of the ion image shown in Figure 1 of the manuscript.

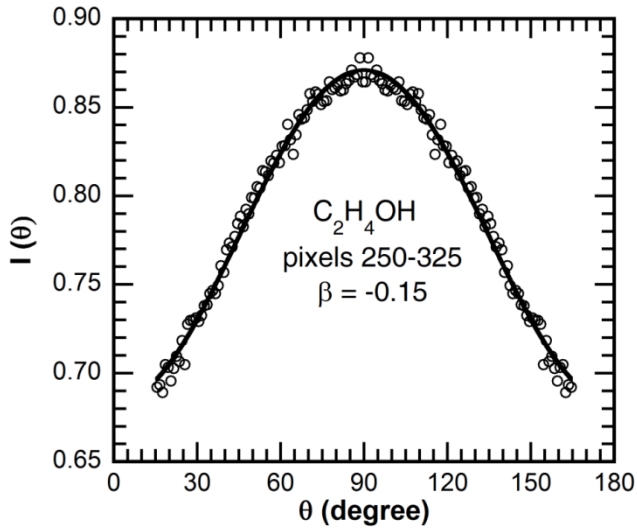

Figure S3

Angular distribution for energetically stable C_2H_4OH radicals detected 250-325 pixels from the center of the ion image shown in Figure 4 of the manuscript.