

An Investigation into the Molecular Dynamics of the Laser Induced Dissociation of
2-Bromoethanol

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Abstract

The unimolecular dissociation of 2-bromoethanol is investigated using computational chemistry methods both to test the reliability of the theories and methods of computational chemistry and to explore the internal mechanism of the dissociation. The dissociation of the bromine ion from 2-bromoethanol was experimentally observed in a previous publication by Ratliff et. al. These experimental results were compared in this thesis to computational calculations of their research. The method of TD-B3LYP proved to be inadequate in this venture except for the lowest energies of the most stable conformer of 2-bromoethanol. However, interesting mechanisms were found such as the formation of HBr as a byproduct of the dissociation.

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Introduction

One of the most researched areas of theoretical chemistry is the study of molecular dynamics. This area of study looks into the inner mechanics of a molecule with the goal of explaining why a molecule behaves the way it is observed to behave. This is often done in the areas of atmospheric chemistry, the chemistry of combustion, and the chemistry of interstellar gases¹⁻³ For this thesis, we are primarily interested in the study of unimolecular photo-dissociation of gaseous 2-bromoethanol visualized by velocity map imaging.¹ This is important because not all molecules decompose in such a way that can be observed well.²

The unimolecular reaction of interest is related to the reaction of the specific molecule 2-bromoethanol reacting with light.¹ When exposed to light of a certain energy (193.3 nm), the bromine atom dissociates from the 2-bromoethanol molecule. This unimolecular decomposition in response to light can be used to help explain other similar reactions that cannot be observed as easily.

Velocity Map Imaging

Velocity map imaging is a 2-D imaging method that can detect and image the impact of fragments on a phosphor screen.^{1,4,5,6} Molecules are released into a vacuum chamber where they pass in front of a laser. The products of the reactants are usually ionized so that a screen at the end of chamber can detect the products of interest with an electric charge. When the products strike the screen, the impact is observed and recorded by a camera.^{1,4} The image gives the distribution of vectors that the products had after the laser induced phenomena. This allows for

the observation of the direction that the products would have after the interaction with the laser in the chamber.

Gaussian Software

One of the most prominent tools of theoretical chemistry is that of computational software.⁷ Computational chemistry software is useful for running the complicated calculations that current quantum mechanical theories provide. This allows for the prediction of experimental data through the theories of molecular dynamics.² One such software program is that of Gaussian 16, which was the program used in the research of this thesis.⁸

Experimental Basis

The basis of this research was an experiment performed in 2010 by Ratliff et. al.¹ In the experiment, a velocity map imaging device was used to observe the unimolecular decomposition of 2-bromoethanol in response to a polarized laser. The velocity map imaging device is pictured in figure 1.

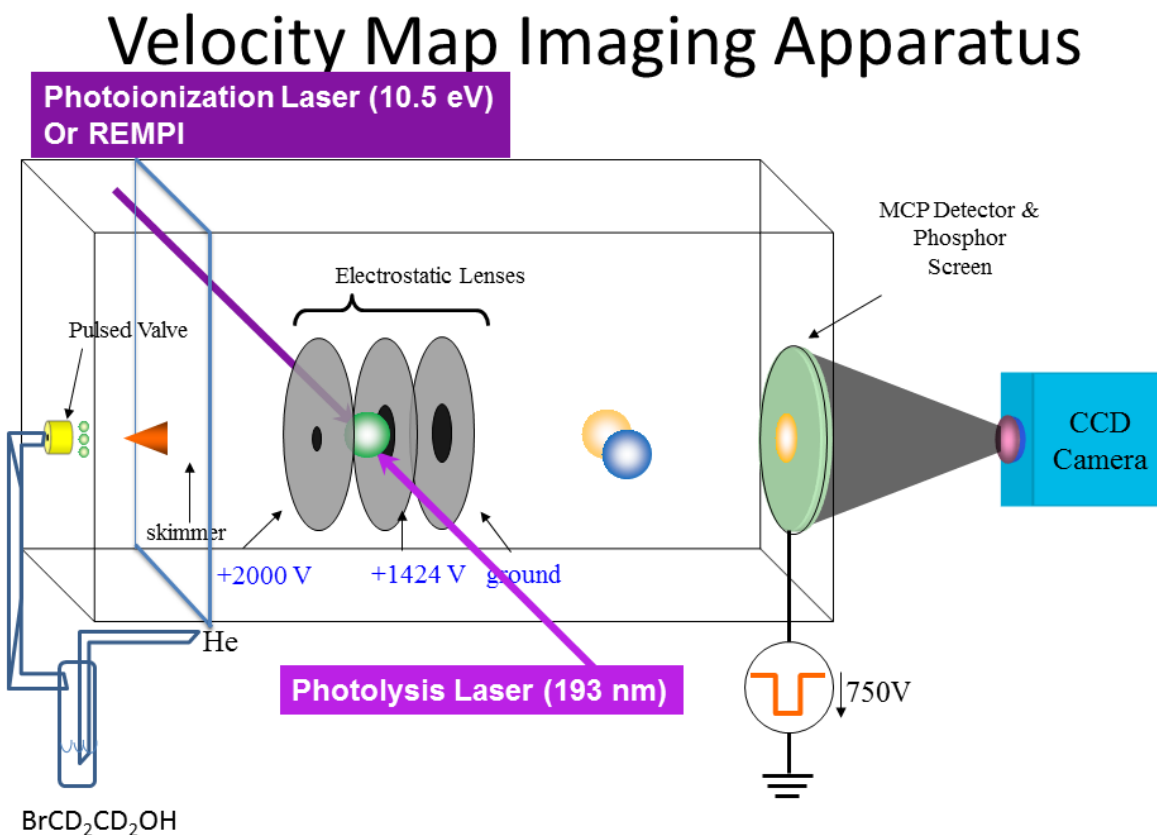


Figure 1. Reprinted with permission.¹ This is a diagram of the velocity map imaging apparatus used in the 2010 experiment by Ratliff et. al. The helium gas passed through the bromoethanol sample can be seen on the bottom left. The lenses as well as the lasers mentioned in the method can be seen in the middle of the chamber. Lastly, the positively charged detector plate and the CCD camera can be seen on the right. The 2-bromoethanol molecules travel from the labeled pulsed valve past the laser. The REMPI (Resonance-enhanced multiphoton ionization) laser is seen at the top. The Br⁻ ions strike the plate in the relative direction from which the Bromine atom dissociated.

Helium was passed through a sample of 2-bromoethanol (see figure 1).¹ This gas mixture passed to a pulsed valve which let out pulses of the gaseous mixture into a chamber under a vacuum. The pressure difference propelled the molecules quickly into the chamber. The spray passed through a focusing lens in order to make the spray a beam of 2-bromoethanol. This beam was passed under a vertically polarized ArF laser with a wavelength of 193.3 nm.¹ The bromine then dissociated from the 2-bromoethanol molecules and a REMPI (Resonance-enhanced multiphoton ionization) laser selectively ionized the Br atoms into Br⁺ ions.⁹ The ion lenses then propel the Br⁺ ions into the phosphor screen. As the ions strike the plate, a CCD camera records the place of impact for the ions which reveals the direction that the Bromine atom left the molecule with reference to the polarized laser.

It is important to note that the group that ran this experiment was interested in a second dissociation that occurred after the Br⁺ dissociated.¹ The research presented in the paper was about the second dissociation. The object of research in this thesis is the first dissociation of the Br⁻ which has not previously been investigated. The research objective of this thesis is original and not in competition with or correcting the research objectives sought by Ratliff et. al.

The results of the experiment can be seen in figure 3.¹ What is important is that if the bromine atom dissociated in a ground electronic state “Br(²P_{3/2}),” the bromine atom would have a direction vector perpendicular to the polarized laser. If the bromine atom was in an excited electronic state “Br(²P_{1/2}),” the atom would dissociate in a direction parallel with the polarized laser. This indicates that there must be a system that determines how the bromine dissociates because it behaves in a consistent and predictable manner. Otherwise, the distribution of bromine

ions would be random. What is very interesting is the complete difference in dissociation based on whether the bromine is in an excited electron state or not.

An important element of the research presented by Ratliff et. al.¹ is the normalized total recoil translational energy distribution for the C-Br bond photo-dissociation in the experiment shown in figure 2. This shows a high kinetic recoil energy of the bromine during the photo-dissociation. This means that the breaking of the C-Br bond was virtually instantaneous. This is a required assumption of this research because the computational research predicts the dissociation of the bromine ion with regard to the polarized laser at the moment of absorption. This cannot be compared to the experimental results if the molecule moves after being stuck by the laser before dissociating as this would cause a different angle to appear in the velocity map imaging apparatus.

The reason this experiment makes such a good candidate for this research is because of the peculiar way bromine dissociates from 2-bromoethanol. Reactions such as this make great candidates because of the lack of understanding of the phenomenon previously.¹⁰ It is the goal of this research to determine if the current quantum mechanical understanding of molecular dynamics is sufficient in predicting or explaining this phenomenon. If it can, this strengthens our belief in the current theories of how molecules operate and we can use this to predict phenomenon in other molecules. If it cannot, then this will show a hole in the current theories of molecular dynamics or the level of theory in the computations. If modern theory can predict something that was discovered after it was developed, it would make great supporting evidence for that level of theory.

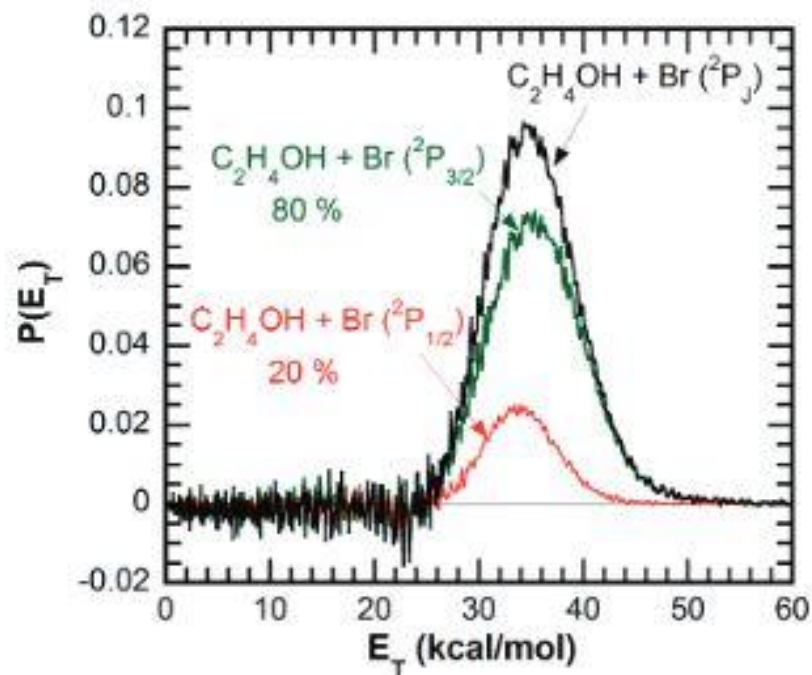


Figure 2. Reprinted with permission.¹ The normalized total recoil translational energy distribution for the C-Br bond photodissociation in the experiment. The black is the sum of the distributions of both the ground state and excited state weighted by their spin-orbit branching ratio of 1:0.26(0.03), respectively. This shows that the energy is great enough to assume that the dissociation is virtually instantaneous.

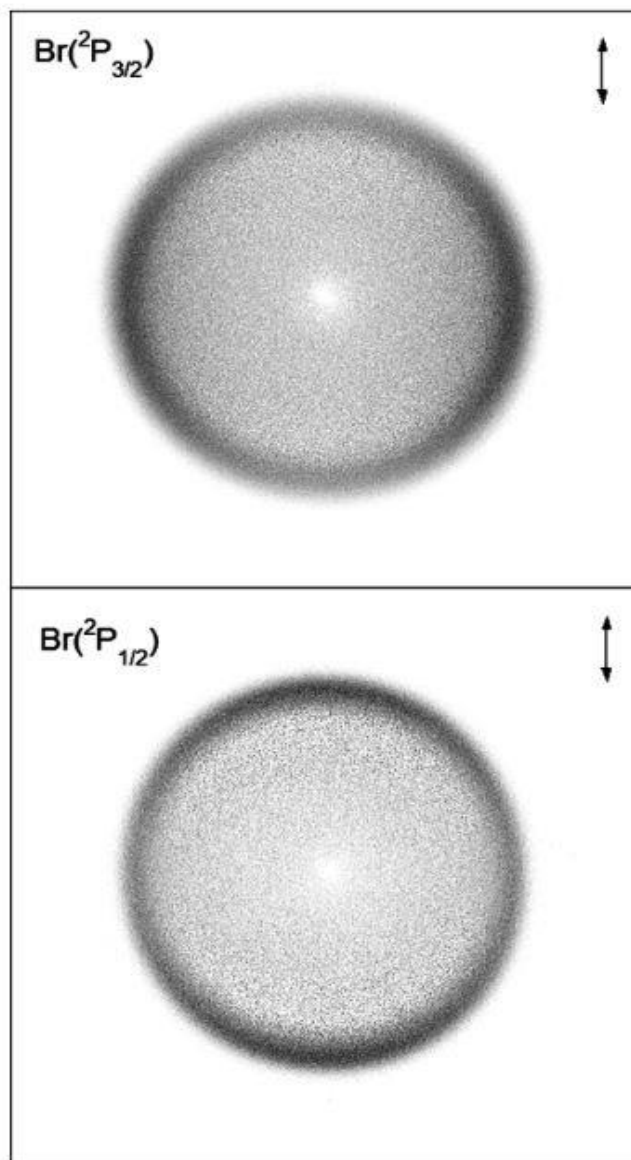


Figure 3. Reprinted with permission.¹ Images of the excited $\text{Br}(^2\text{p}_{1/2})$ and ground $\text{Br}(^2\text{p}_{3/2})$ state bromine ions detected with 2+1 REMPI following the photodissociation of 2-bromoethanol at 193 nm. The photo dissociation laser was polarized along the vertical plane of the image, as the arrows indicate. Each image is 901×901 pixels and was background subtracted by subtracting the images obtained with 193 nm only and 234 nm only from the raw data. The dark areas on the edge of the images represent the Br^- ions striking the plate.

Excited Electron States

When a molecule absorbs a photon, its electrons enter what is called an excited electron state. This is when the electrons farthest from the nucleus move into a higher orbital leaving an orbital gap. These electrons are defined as leaving the highest occupied molecular orbital (HOMO) and entering the lowest unoccupied molecular orbital (LUMO). This is the process that causes the C-Br bond to stretch.^{1,11,12} Photon wavelengths of 193.3 nm commonly excite small organic molecules with C-Br.^{1,13} The HOMO and LUMO of both conformers of 2-bromoethanol can be seen in figures 4 and 5. All orbital calculations were run using B3LYP/6-31G theory/basis set. A very simple basis was used because the orbital calculations were run for illustration purposes only.

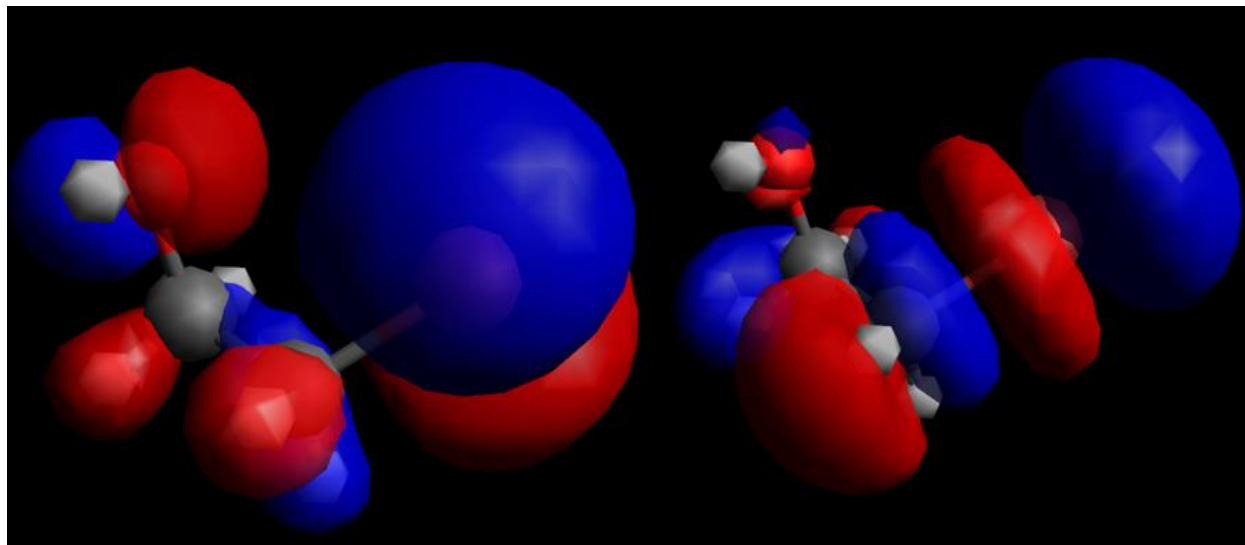


Figure 4. A visual representation of the HOMO (left) and LUMO (right) of the gauche conformer of 2-bromoethanol. When the molecule absorbs the photon, the electrons in the clouds on the left excite to the clouds on the right. The molecule is in the same position in both images except that the right is slightly more zoomed out. The C-Br bond is shown in the front with the

bromine on the upper right so the bond that breaks during the dissociation is the most visible.

Images were produced using Avogadro © 2018 Avogadro Chemistry.

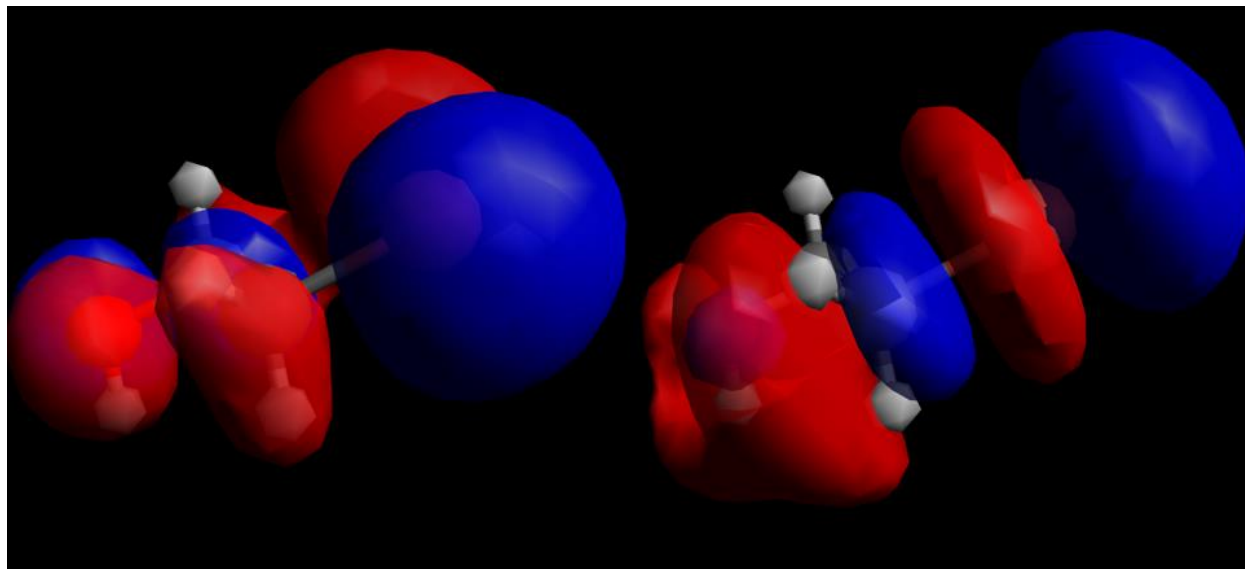


Figure 5. A visual representation of the HOMO (left) and LUMO (right) of the trans conformer of 2-bromoethanol. When the molecule absorbs the photon, the electrons in the clouds on the left excite to the clouds on the right. The molecule is in the same position in both images. The C-Br bond is shown in the front with the bromine on the upper right so the bond that breaks during the dissociation is the most visible. For reference, the oxygen is in the lower left. Images were produced using Avogadro © 2018 Avogadro Chemistry.

Method

The primary way we can calculate the excited state energies and other molecular qualities given by modern theoretical chemistry is through computational simulation. For this research ©Gaussian 16 computational chemistry software was used.⁸

The simulations were performed on both the gauche and trans forms of 2-bromoethanol since these are the two most stable conformers of the molecule (see figures 6 and 7). These are also the only stable conformers of 2-Bromoethanol.

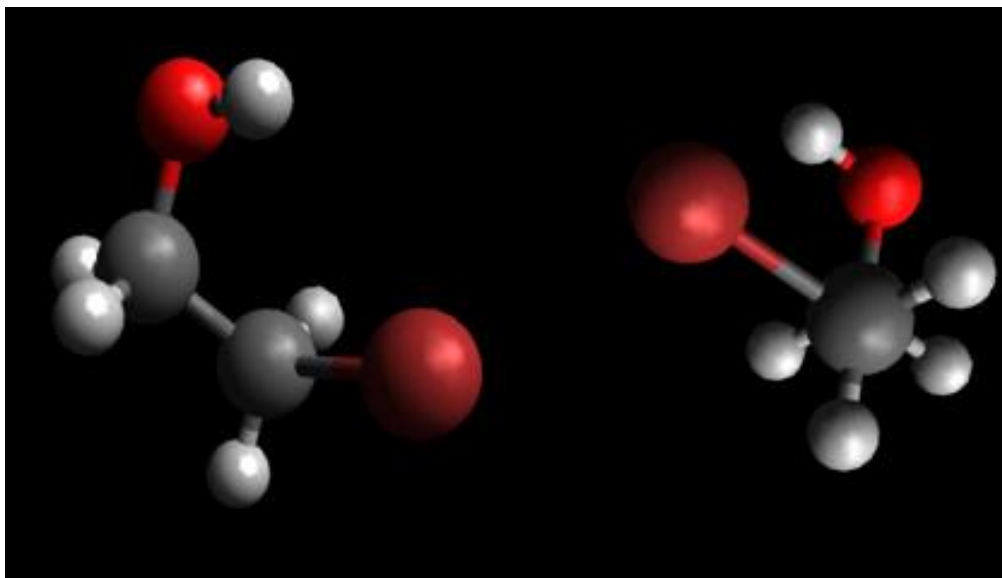


Figure 6. Reprinted with permission.¹⁵ The gauche conformer of 2-bromoethanol seen from two different angles. This conformer is defined by the oxygen atom having a 60° angle from the bromine atom when viewed down the carbon-carbon bond. Atom legend: white=hydrogen, red=oxygen, dark red=bromine, grey=carbon.

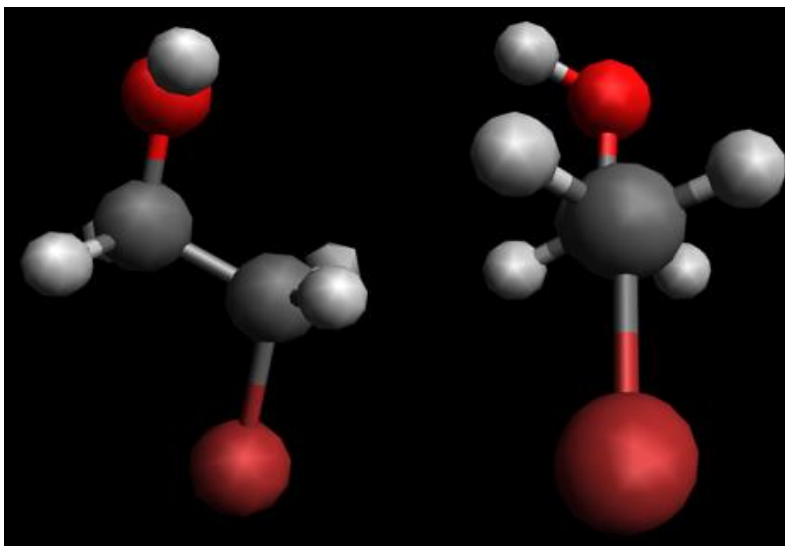


Figure 7. The trans conformer of 2-bromoethanol seen from two different angles. This conformer is defined by the oxygen atom having a 180° angle from the bromine atom when viewed down the carbon-carbon bond. Atom legend: white=hydrogen, red=oxygen, dark red=bromine, grey=carbon.

Throughout the experiment the theory/basis set used was B3LYP/6-31G(d).⁸ B3LYP was the theory used for all calculations in this thesis because of its balance of high speed and high accuracy.¹⁴ The following method was performed for both the gauche and trans conformers.

The first step was to run an optimization to determine the exact bond lengths and angles that produce the lowest energy and therefore the most stability. After determining this, a relaxed optimization was run with the given bond angles and lengths except the bromine carbon bond was fixed. This was done to find the most stable configurations of the molecule as the bromine dissociated. The lengths calculated were from 1.0 to 5.0 Å in 0.1 Å intervals. Then TD-B3LYP was used to calculate the exact excited state energies of the different optimized parameters.⁸ TD stands for time-dependent and means that the calculations are run with regard to time-dependent variables such as magnetic fields.¹⁸ Time-dependent calculations are necessary when running

calculations for a molecule in specific set of initial conditions.¹⁹ With this data, the electronic dipole moment was also calculated at each conformer most stable position.

The angle between the electronic dipole moment and the C-Br bond was also calculated. This was done by taking the simulation given position vectors of bromine and carbon-2. The difference between these vectors was the C-Br vector. The electronic dipole moment vector was given by the computational results. The angle between these two vectors was determined using the formula: $Angle = \left(\frac{180^\circ}{\pi}\right) * \left(\frac{\textit{The Cross Product of the Vectors}}{\textit{The Norm of C-Br Vector} * \textit{The Norm of the Dipole Moment Vector}}\right)$.

The trans conformer was then recalculated after observing the results of the first calculation (discussed in results and discussion). A more thorough but more time-consuming basis set was used to make sure the results of the first calculation were not just caused by an insufficient basis set. The new basis set used was “6-311++G(3df,2p)”. All the excited energy state and electronic dipole moment angle calculations for the trans conformer were recalculated using this basis set. This specific basis set was chosen because of its previous use on similar molecules that are more complicated than 2-bromoethanol.³

Results

Gauche Conformer of 2-Bromoethanol

The results of the original optimization of the gauche conformer can be seen in figure 6. Figure 8 presents the ground and excited energy states of the molecule with regard to C-Br bond length. All energy is represented as kcal/mol in the example set by peer reviewed papers.¹⁷

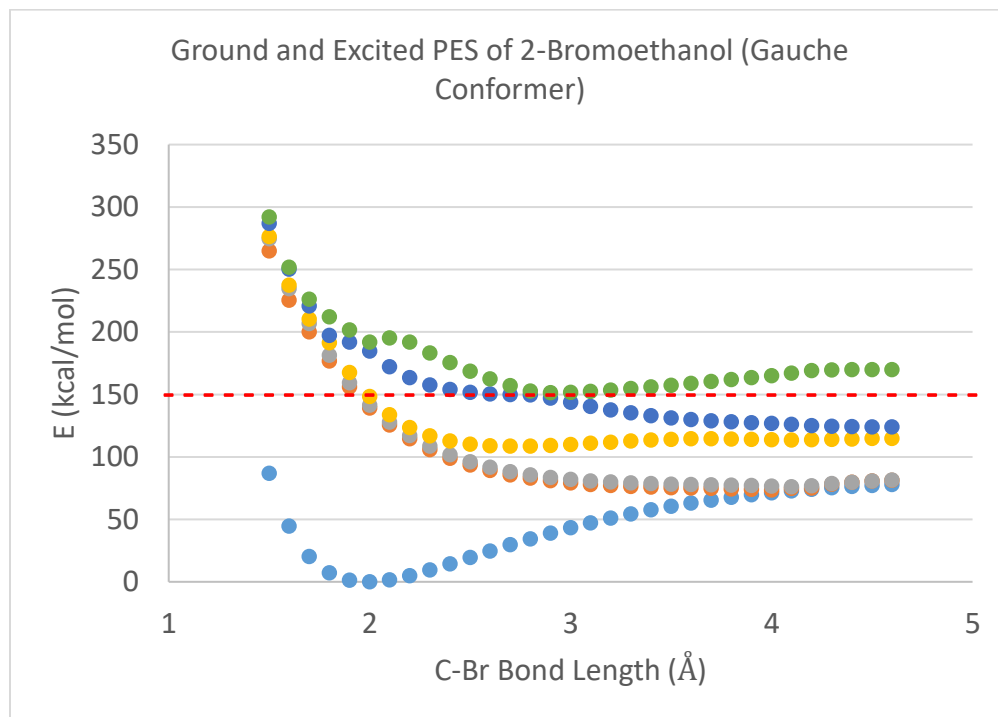


Figure 8.¹⁵ These are the potential energy surfaces (PES) in kcal/mol of the gauche conformer of 2-bromoethanol in its ground and excited electron states. The lowest blue curve is the ground state and the rest are the different excited electron states. The energy of a 193.3 nm photon is provided for reference. Legend: Blue=Ground State, Orange= 1st Excited State, Grey= 2nd Excited State, Yellow= 3rd Excited State, Dark Blue= 4th Excited State, Green= 5th Excited State, Red= Energy of the 193.3 nm Photon.

Notice for the ground state PES that the lowest energy is at about 2 Å in C-Br bond length. This is expected in the ground state because the molecule is stable and not dissociating before the molecule is energized. When a photon hits the molecule, the molecule is excited into the Franck-Condon region where the electrons reach one of the excited states seen in the graph. As can be seen, the lowest energy for the excited states stretches the C-Br bond out to dissociate the bond. Something of note is that the excited state curves primarily converge into two main

points. One is at the ground state of the molecule at greater than 4.0 angstroms while the other convergence has significantly higher energy.

The green line's convergence can be ignored. It is presented to show that the energy states above the 4th excited energy state do not have slopes that would lead to dissociation along the C-Br bond. Because the 5th and above energy states do not have a steep energy slope, they are not the energy states that caused the observed dissociation in the basis experiment. Only excited energy states 1-4 give a proper dissociation slope.

Excited energy states 1-4 cause dissociation with 1 and 2 leaving the molecule in the ground energy state and 3 and 4 leaving the molecule in an excited energy state. This corresponds with the excited and ground state bromines observed in the experiment by Ratliff et al.¹

The resulting angles between the electronic dipole moment vectors and the carbon bromine vectors are presented in figure 6.

Table 1. The Relative Angle of the Electronic Dipole Vector for the Different Excited States of Gauche 2-Bromoethanol

Excited Electron State	$\theta_{C-Br,\mu}$
1	89.3
2	55.9
3	110.9
4	160.6
5	116.7

The different excited electron states for gauche 2-bromoethanol and the resulting angle (θ) between the C-Br vector and the electronic dipole moment vector (μ) in degrees.¹⁵

The significance of these angles is that they represent the angle from which the bromine leaves the molecule relative to the polarized laser. The electronic dipole moment vector is the direction from which 2-bromoethanol can absorb a photon to that specific excited energy state. Every excited energy state has a specific electronic dipole moment vector. A photon can only excite a molecule to an excited energy state if the photon strikes the molecule in the direction of that excited state's electronic dipole moment vector. As mentioned earlier, the dissociation was assumed to be instantaneous. Therefore, at the moment of dissociation, the electronic dipole moment must be aligned with the vertically polarized laser. Therefore, the angle of the C-Br bond from the angle of the electronic dipole moment will be the angle from the polarized laser that the bromine ion will dissociate from the molecule.

Trans Conformer of 2-Bromoethanol

6-31G(d) Basis Set.

The results of the original optimization of the trans conformer can be seen in figure 7. Figure 9 presents the ground and excited energy states of the molecule compared to the C-Br bond length for the simpler basis set of 6-31G(d).

The results for this seemed reasonable at first but the 3rd (yellow) excited energy state and the resulting electronic dipole moment angles gave some concern as to the ability of the 6-31G(d) basis set. This will be explained more in the discussion. The calculated angles between the C-Br vector and the electronic dipole moment vector are provided in Table 2.

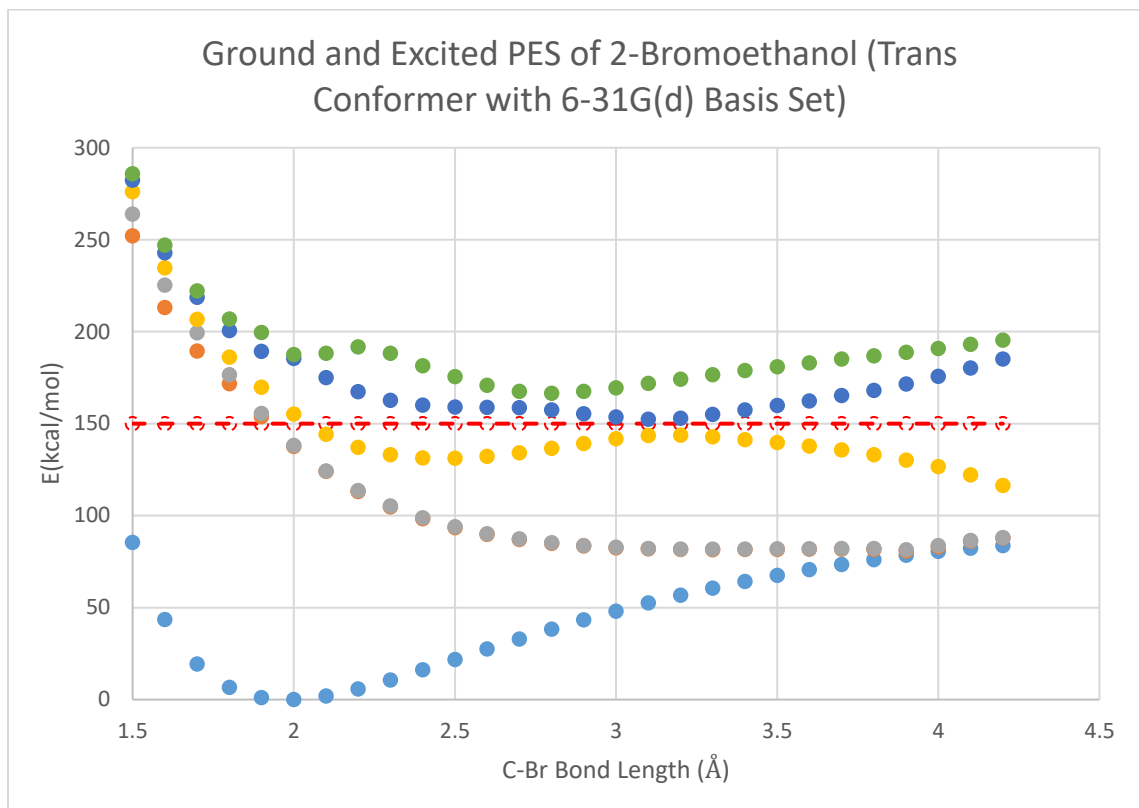


Figure 9. The potential energy surfaces (PES) in kcal/mol of the trans conformer of 2-bromoethanol in its ground and excited electron states. This data was calculated using the basis set 6-31G(d). The lowest blue curve is the ground state and the rest are the different excited electron states. The energy of a 193.3 nm photon is provided for reference. Legend: Blue=Ground State, Orange= 1st Excited State, Grey= 2nd Excited State, Yellow= 3rd Excited State, Dark Blue= 4th Excited State, Green= 5th Excited State, Red= Energy of the 193.3 nm Photon.

Table 2. The Relative Angle of the Electronic Dipole Vector for the Different Excited States of Trans 2-Bromoethanol

<i>Excited Electron State</i>	$\theta_{C-Br,\mu}$
1	28.3
2	154.5
3	158.3
4	147.2
5	164.6

The different excited electron states for trans 2-bromoethanol and the resulting angle (θ) between the C-Br vector and the electronic dipole moment vector (μ) in degrees.

6-311++G(3df,2p) Basis Set.

The results of using the more advanced basis set of 6-311++G(3df,2p) used to calculate the excited electron states of the trans conformer can be seen in figure 10. The new angles given by these calculations can be seen in Table 3.

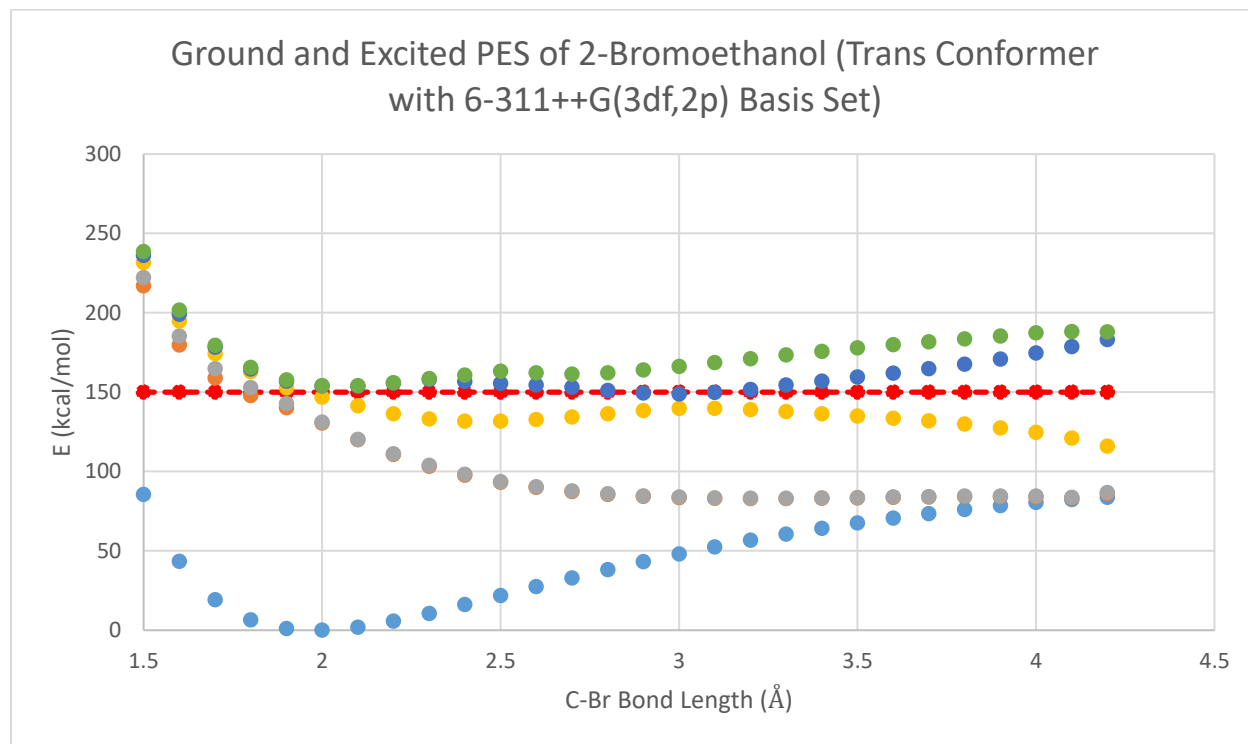


Figure 10. The potential energy surfaces (PES) in kcal/mol of the trans conformer of 2-bromoethanol in its ground and excited electron states. This data was calculated using the basis set 6-31G(d). The lowest blue curve is the ground state and the rest are the different excited electron states. The energy of a 193.3 nm photon is provided for reference. Legend: Blue=Ground State, Orange= 1st Excited State, Grey= 2nd Excited State, Yellow= 3rd Excited State, Dark Blue= 4th Excited State, Green= 5th Excited State, Red= Energy of the 193.3 nm Photon.

Table 3. The Relative Angle of the Electronic Dipole Vector for the Different Excited States of Trans 2-Bromoethanol with New Basis Set.

Excited Electron State	$\theta_{C-Br,\mu}$
1	56.6
2	116.7
3	150.0
4	119.3
5	119.2

The different excited electron states for trans 2-bromoethanol and the resulting angle (θ) between the C-Br vector and the electronic dipole moment vector (μ) in degrees.

Something else of value is that the lowest ground state PES scan for the gauche conformer came to -2726.1413 hartrees and for the trans conformer came to -2726.1378 hartrees. This puts the Gauche conformer at a lower energy and is more stable. Therefore, it is more statistically likely that the molecule will be in the gauche conformer over the trans conformer at any given moment in time provided that the level of theory calculated is accurate for this molecule.

Formation of HBr

An accidental discovery was made during the calculations. While optimizing 2-bromethanol with a C-Br bond length past 4 angstroms, there was a sudden drop in in the potential energy scan for both conformers. This was observed to be a problem and it was determined that one of the hydrogens was leaving the ethanol during dissociation and joining the bromine to form HBr. This was assumed to be a mistake until it was seen that HBr was one of the byproducts found from the experiment.¹ It was previously unknown why this byproduct

formed to in the experiment. These calculations show that if one of the hydrogens had enough energy to leave the ethanol (the exact hydrogen varied between the conformers), they would attach to the bromine because that formed a system of less energy which means it is more stable.

Illustrations for these transitions are given in figures 9 and 10.

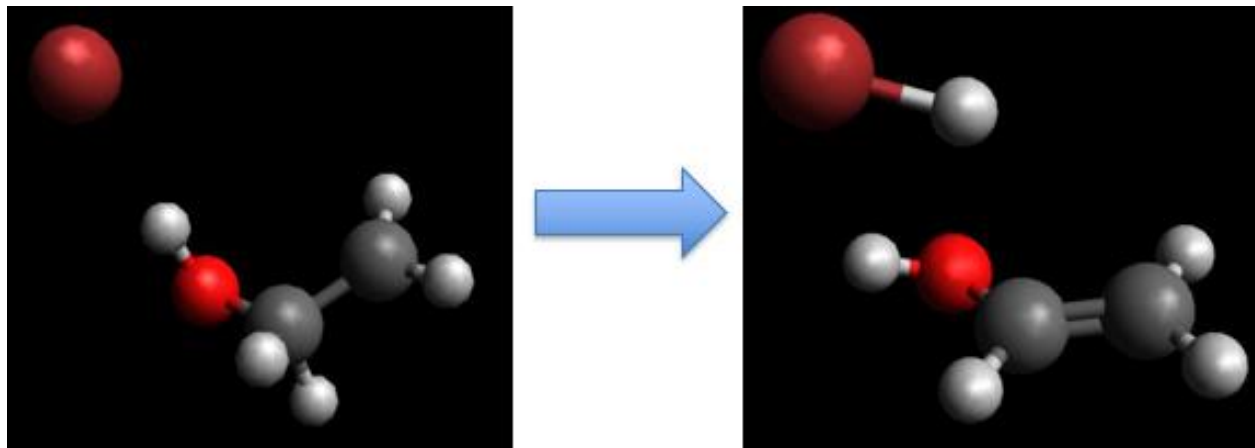


Figure 11. The illustration of the gauche conformer of 2-bromoethanol as it undergoes the hydrogen shift that creates the HBr. In this case, it leaves ethanol behind as a double carbon-carbon bond forms. Atom legend: white=hydrogen, red=oxygen, dark red=bromine, grey=carbon.

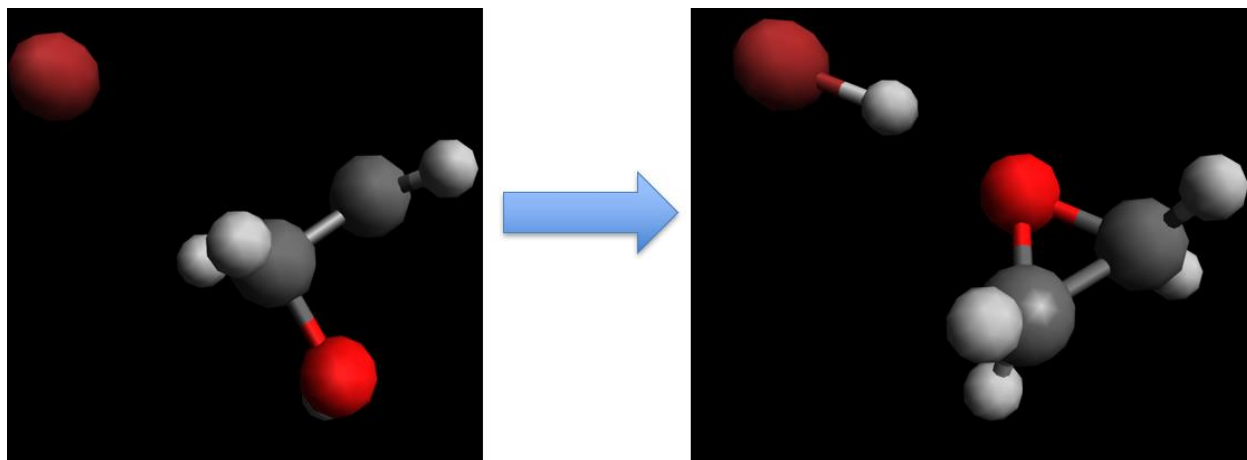


Figure 12. The illustration of the trans conformer of 2-bromoethanol as it undergoes the hydrogen shift that creates the HBr. Unlike the gauche conformer, it leaves an epoxide behind as a triangle shape is formed with the bonds between the two carbons and the oxygen. Atom legend: white=hydrogen, red=oxygen, dark red=bromine, grey=carbon.

Discussion

Excited Electronic States

The electronic state data from this experiment was illuminating. The data from the gauche calculations provide both a path for the ground state dissociation in the 1st and 2nd excited electron states and one for the excited dissociation in the 3rd and 4th energy states. This shows an equal opportunity for the photon to cause both a ground state and excited state bromine dissociation. As stated before, the 5th excited electronic state and up are do not lead to C-Br cleavage. So, these are not considered to be part of the process.

The data from the trans conformer using the 6-31G(d) basis produced results that had not been expected. The 1st and second excited electron states do form a fast dissociation curve, but the 3rd forms an odd curve that was not expected. This curve seems to have some stability in the Frank-Condon region which would make it a very bad dissociation curve. This would imply that there is no excited electron dissociation state for the trans conformer. After seeing the electronic dipole moment angles, there is a good chance that the basis set used may have been too small and simple for the simulation of the process. This is why the more complex basis set was used to recalculate the excited energy states.

The recalculated excited electronic states only show significant difference for the 4th and 5th excited states below 2 angstroms of the C-Br bond length. This difference is not a significant

one to this research. The main confusion was caused by 3rd electronic state and its odd shape remained even with the more complex basis set. It is possible that the trans conformer primarily only gives the ground state bromine ions. This would be in line with the experiment since there was a higher proportion of ground state bromine ions to excited ones.¹

Electronic Dipole Moment Vector Angles

The angles given for the gauche confirmation seem to both agree and disagree with the experimental data. The angle of 89.3 degrees is almost perfect since it is a ground state dissociation and was observed in the experiment to have a perpendicular dissociation to the polarized laser. The 160.6 degrees of the 4th state is also encouraging since it is near parallel to the polarization as was observed for an excited state dissociation. The other two have angles that do not at all line up with the experimental results. There are a couple explanations for this. One is that the calculations was incorrect or that the method or basis set used was insufficient. Another is that this is a hole in the current theories of chemistry. The final option is that the 2nd and 3rd electronic states are not, or rarely are, actually reached in the experiment. This would assume that for some reason, the molecule was only being excited into the 1st or 4th excited electron states. This doesn't quite agree with the graph which places excited states 1-3 in the energy range of the photon when the molecule is in its most stable state while the 4th remains outside of it.

The angles for the 6-31G(d) basis set calculation for the trans conformer really do not appear to be anything like the angles observed in the experiment. The worst being the 2nd excited electron state since it shows an angle much more similar to being parallel with the polarized laser than perpendicular to it. This is either a broad and unprecedented failure of the program which is

unlikely, or the method or basis set is insufficient for the calculation. Since the B3LYP method is already one of the more thorough methods, a better basis set was used.

The angles given for the electronic dipole moment of the trans conformer with the new basis set are an improvement over the previous calculations. That being said, they are not that good. The angle for the 1st excited state at 56.6 degrees is technically closer to 90 than 0 unlike the previous angle, but it is still a long way from being perpendicular. The 3rd excited state's angle at 150.0 degrees has the same issue where it is closer to 180 than the last calculation but still far off. So the angles showed significant improvement, but they are still far from the experimental results.

Formation of HBr

The prediction of the formation of HBr greatly increases the reliability of the methods used. This doesn't say much for the calculations for the excited electric states, but it does demonstrate the reliability of the B3LYP/6-31G(d) theory/basis set in predicting the lowest energy conformers of small molecules. This helps to show that the methods and theory used is in fact reliable and has good results. This builds credibility towards the other results presented in this thesis.

Future Possibilities

The project has some new ways it could be taken. One of these ways would be to run the same calculations again and vary the theories and basis sets used to see if any match the results of the experiment better than the ones used in this research. This would examine the reliability and consistency of different levels of computational chemistry.

Another possibility is the exploration of the mechanism for the creation of HBr. The successful prediction of this byproduct could be an interesting insight into the mechanism of how it formed. It could also give some useful information on the chemical reactions caused by the absorption of a proton.

It would also be worthwhile try methods other than TD-B3LYP to calculate the excited energy states. The differing results given by other methods such as EOMCCSD and CAS could show that one of them produces results closer to the experimentally observed results by Ratliff et. al.

Conclusion

The only concrete conclusion that can be drawn from these results is that the TD-B3LYP method is only accurate to predict the energy and electronic dipole moment vector of the 1st excited state for the most stable confirmation of the molecule. Some other details looked good in the gauche such as the 4th excited state and the grouping of the dissociation curves into two groups. Other than that, the results were all over the place. Before this can be called a failure of modern theory, it must be tested in methods even more complex than the ones used in this research. Rather, this is a failure of this level of theory. The methods, theories, and basis sets used in this research proved to be inadequate to predict the behavior of the unimolecular dissociation of 2-bromoethanol with the exception of low energy states in the most stable conformer.

References

- ¹Ratliff, B. J.; Womack, C. C.; Tang, X. N.; Landau, W. M.; Butler, L. J.; Szpunar, D. E. Modeling the Rovibrationally Excited C₂H₄OH Radicals from the Photodissociation of 2-Bromoethanol at 193 Nm. *The Journal of Physical Chemistry A*, **2010**, 114 (14), 4934–4945.
- ²Barone, V.; Improta, R.; Rega, N. Quantum Mechanical Computations and Spectroscopy: From Small Rigid Molecules in the Gas Phase to Large Flexible Molecules in Solution. *Acc Chem Res*, **2008**, 39, 605 - 616.
- ³Brynteson, M. D.; Butler L. J. Predicting the Effect of Angular Momentum on the Dissociation dynamics of Highly Rotationally Excited Radical Intermediates. *J. Chem. Phys*, **2015**, 142, 054301 1-13.
- ⁴Heck, A. J. R.; Chandler, D. W. Imaging Techniques for the Study of Chemical Reaction Dynamics. *Annu. Rev. Phys. Chem*, **1995**, 46, 335-372.
- ⁵Ren, Y.; Qin, Z.; Wang, H.; Zheng, X.; Cui, Z. An Approach for Improving Signal-to Noise Ratio in Photoelectron Velocity Map Imaging Experiments. *Journal of Electron Spectroscopy and Related Phenomena*, **2018**, 222, 5-9.
- ⁶Baeza-Romero, M. T.; Blitz, M. A.; Goddard, A.; Seakins, P. W. Time-of-Flight Mass Spectrometry for Time-Resolved Measurements: Some Developments and Applications. *Int. J. Chem. Kinet*, **2012**, 44, 532-545.
- ⁷Young, D.C. (2002). *Other Chemical Properties*. In *Computational Chemistry*, D.C. Young (Ed.). doi:10.1002/0471220655.ch13 pg.113.
- ⁸Gaussian. About Gaussian 16. <http://gaussian.com/g16main/> (accessed Oct 2, 2018).

- ⁹Hosaka, K.; Itakura, R.; Yokoyama, K.; Yamanouchi, K.; Yokoyama A. Photoelectron-Photoion Coincidence Momentum Imaging for Dissociative Ionization of Ethanol in Intense Laser Fields. *Chemical Physics Letters*, **2009**, 475, 19-23.
- ¹⁰Scrape, P. G.; Roberts, T. D.; Lee, S. H.; Butler, L. J. Dissociation Pathways of the CH₂CH₂ONO Radical: NO₂ + Ethene, NO + Oxirane, and a Non-Intrinsic Reaction Coordinate HNO + Vinyloxy Pathway. *J. Phys. Chem. A*, **2016**, 120, 4973-4987.
- ¹¹Fraser, G. T.; Pate, B. H.; Bethardy, G. A.; Perry, D. S. Frequency-Resolved Measurement of Fast Intramolecular Vibrational Energy Redistribution (IVR) in the O-H Stretch of Gas-Phase Ethanol. *Chemical Physics*, **1993**, 175, 223-236.
- ¹²Anh, N.T. (2007). *Some Structural Problems*. In *Frontier Orbitals*, N.T. Anh (Ed.).
doi:10.1002/9780470065709.ch7.
- ¹³Wang, L.; Scrape, P. G.; Roberts, T. D.; Joshi, P. P.; Butler, L. J. Competing C-Br and O-NO Photofission upon Excitation of BrCH₂CH₂ONO at 193 nm. *J. Phys. Chem. A*, **2015**, 119, 12005-12014.
- ¹⁴Zimmermann, M. M. D. (2011). *A physical chemist's guide to applied computational chemistry: Practical calculation of polyprotic acid pKa values, mercury halides, thiols, and methylmercury analogues' stabilities and structures, and raman spectra of myo-inositol hexakis phosphate* (Order No. 3474019). Available from ProQuest Dissertations & Theses Global. (896912378). Pg. 68.
- ¹⁵French, K. A.; Arntz, G. M.; Brynteson, M. *Theoretical Studies on the Transition Dipole Moments of Bromoethanol*. Poster. **2019**. Liberty University.

- ¹⁶Brynteson, M. D.; Womack, C. C.; Booth, R. S.; Lee, S. H.; Lin, J. J.; Butler L. J. Radical Intermediates in the Addition of OH to Propene: Photolytic Precursors and Angular Momentum Effects. *J. Phys. Chem. A*, **2014**, 118, 3211-3229.
- ¹⁷Vargas-Caamal, A.; Ortiz-Chi, F.; Moreno, D.; Restrepo, A.; Merino, G.; Cabellos, J. L. The Rich and Complex Potential Energy Surface of the Ethanol Dimer. *Theor. Chem. Acc*, **2015**, 134:16, 1-9.
- ¹⁸Skouteris D. Time-dependent calculations on systems of chemical interest: Dynamical and kinetic approaches. *International Journal of Quantum Chemistry*, **2016** 116(22):1618-1622. doi:10.1002/qua.25233.
- ¹⁹Ullrich, Carsten A. *Time-Dependent Density-Functional Theory: Concepts and Applications*; Oxford University Press: New York, 2012; 7. <https://ebookcentral-proquest-com.ezproxy.liberty.edu/lib/liberty/reader.action?docID=829457&ppg=5>.