

Supplemental Material: **Analyzing angular distributions for two-step dissociation mechanisms in velocity map imaging**

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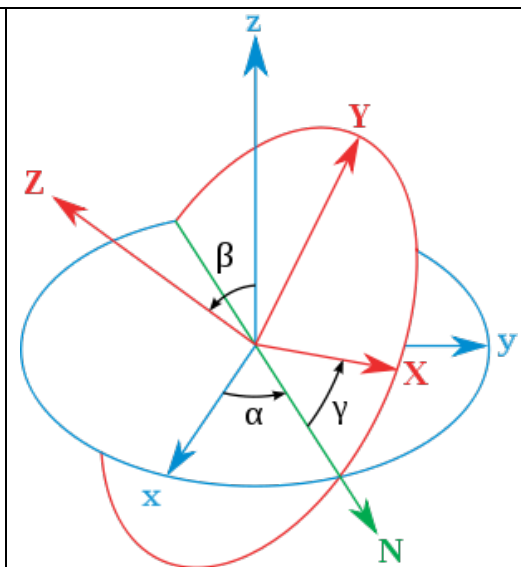
A. Euler Angles and Transformations of Coordinate 3-Space

Define the three rotations they show on the Wiki web page animation for Euler angles:

$T_z(\alpha)$ = rotate by an angle α about the **z-axis**
This moves what was a vector along the **x** axis to a new position, the **vector N** (line of nodes).

$T_N(\beta)$ = rotate by an angle β about fixed **vector N**
This moves what was a vector along the **z-axis** to a new position, the **Z-axis**.

$T_z(\gamma)$ = rotate by an angle γ about the **Z-axis**
This moves what was a vector along the **vector N** to a new position, the **X-axis**.



Since the unit vectors along the coordinate axes of the blue coordinate system are:

$\hat{x} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, $\hat{y} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ and $\hat{z} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$. Let's call the vector v , written in the blue coordinate system basis, $v_{[\hat{x}, \hat{y}, \hat{z}]}$.

Likewise, let's call the SAME vector v , but written in the red coordinate system basis, $v_{[\hat{X}, \hat{Y}, \hat{Z}]}$. We wish to derive the matrix A that changes the coordinates of v in the $[\hat{x}, \hat{y}, \hat{z}]$ coordinate system to the coordinates of v in the $[\hat{X}, \hat{Y}, \hat{Z}]$ coordinate system.

$$v_{[\hat{X}, \hat{Y}, \hat{Z}]} = A v_{[\hat{x}, \hat{y}, \hat{z}]}$$

The matrix T given in eqn. 8 of the paper is A^{-1} , as our code requires converting the coordinates of a vector in the red coordinate system to its coordinates in the blue coordinate system.

The red coordinate system is obtained from the blue coordinate system by executing the following rotations in the order given:

$T_z(\alpha)$ = rotation by an angle α about the **z axis** (right hand rule gives direction)

$T_N(\beta)$ = rotation by an angle β about the **N, the line of nodes**

$T_z(\gamma)$ = rotation by an angle γ about the **Z axis**.

Note: The transformation $T_z(\alpha)$ here does not equal the matrix transformation $R_z(\alpha)$ used in mathematical methods texts such as that by Arfken. The matrix $R_z(\alpha)$ in Arfken is actually $(T_z(\alpha))^{-1}$, a matrix for a rotation by $-\alpha$ around the **z-axis**. To see how $R_z(\alpha) = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$ rotates a vector, let it rotate $\hat{x} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ to see what it does. $\begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos \alpha \\ -\sin \alpha \\ 0 \end{pmatrix} = \begin{pmatrix} \cos -\alpha \\ \sin -\alpha \\ 0 \end{pmatrix}$. Thus, $R_z(\alpha)$ rotates by an angle $-\alpha$ about the fixed **z axis**. A geometric derivation (courtesy of Lynne Butler) for the formula for A in terms of the Euler angles follows. The final matrix A is the same as in <http://mathworld.wolfram.com/EulerAngles.html> but the derivation given below uses the physical transformations that rotate vectors, like $T_z(\alpha)$, connecting more clearly with the Wiki animation http://en.wikipedia.org/wiki/Euler_angles

The coordinates of **N**, a vector along the line of nodes, is $N = \begin{pmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{pmatrix}$ with α as shown in

the figure above. If we rotate $\hat{x} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ by an angle α about the **z axis**, the new vector

should be $N = \begin{pmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{pmatrix}$. Calculating $T_z(\alpha)\hat{x} = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{pmatrix}$ Good.

So the code in our paper needs to calculate the coordinates of a vector **v** in the red coordinate system, if we are given the coordinates of **v** in the blue coordinate system.

To begin the derivation of the expression for A given in eqn. 8 of the paper, let's define a few matrices:

$T_z(\alpha)$ = rotation by an angle α about the **z axis**

$$= \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$T_x(\beta)$ = rotation by an angle β about the **x axis**

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \beta & -\sin \beta \\ 0 & \sin \beta & \cos \beta \end{pmatrix}$$

And one more we need badly:

$T_N(\beta)$ = rotation by an angle β about **N**, a vector along the line of nodes

Importantly this rotation matrix is the product of three matrices we have already introduced:

$$T_N(\beta) = T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1}$$

To see that this is true, consider that $\mathbf{N} = T_z(\alpha) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$.

Clearly, a rotation by the angle β about \mathbf{N} should leave the **vector** \mathbf{N} unchanged. So let's see if the matrix $T_N(\beta) = T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1}$ does this below.

$$\begin{aligned} T_N(\beta) \mathbf{N} &= T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1} \mathbf{N} \\ &= T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1} T_z(\alpha) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ &= T_z(\alpha) T_x(\beta) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ &= T_z(\alpha) \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \beta & -\sin \beta \\ 0 & \sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ &= T_z(\alpha) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ &= \mathbf{N} \quad \text{Good.} \end{aligned}$$

Finally, we need the final rotation described above, $T_z(\gamma)$. The unit vector along the **Z-axis** is calculated by beginning with a unit vector on the **z axis**, $\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$, then executing a rotation of α about the **z axis**, $T_z(\alpha)$, then a rotation of an angle β about the line of nodes, $T_N(\beta)$. So $\hat{\mathbf{Z}} = T_N(\beta) T_z(\alpha) \hat{\mathbf{z}}$. Thus a rotation through an angle γ around the **Z axis**, with a similar argument as that above for $T_N(\beta)$, is:

$$T_z(\gamma) = T_N(\beta) T_z(\alpha) \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} (T_N(\beta) T_z(\alpha))^{-1}$$

Let's rewrite this:

$$T_z(\gamma) = T_N(\beta) T_z(\alpha) \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} (T_N(\beta) T_z(\alpha))^{-1}$$

$$\begin{aligned}
&= T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1} T_z(\alpha) \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} (T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1} T_z(\alpha))^{-1} \\
&= T_z(\alpha) T_x(\beta) \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} (T_z(\alpha) T_x(\beta))^{-1} \\
&= T_z(\alpha) T_x(\beta) T_z(\gamma) (T_z(\alpha) T_x(\beta))^{-1}
\end{aligned}$$

So the matrix that maps the unit vectors along the blue coordinate axes, \hat{x} , \hat{y} and \hat{z} to the unit vectors along the red coordinate axes \hat{X} , \hat{Y} , and \hat{Z} is the product $T = T_z(\gamma) T_x(\beta) T_z(\alpha)$. We get a simple expression for T below:

$$\begin{aligned}
T_z(\gamma) T_x(\beta) T_z(\alpha) &= T_z(\gamma) T_z(\alpha) T_x(\beta) (T_z(\alpha))^{-1} T_z(\alpha) \\
&= T_z(\gamma) T_z(\alpha) T_x(\beta) \\
&= T_z(\alpha) T_x(\beta) T_z(\gamma) (T_z(\alpha) T_x(\beta))^{-1} T_z(\alpha) T_x(\beta) \\
&= T_z(\alpha) T_x(\beta) T_z(\gamma)
\end{aligned}$$

Finally, we find the matrix A that changes the coordinates of a vector v in the $[\hat{x}, \hat{y}, \hat{z}]$ coordinate system to the coordinates of v in the $[\hat{X}, \hat{Y}, \hat{Z}]$ coordinate system.

$$v_{[\hat{X}, \hat{Y}, \hat{Z}]} = A v_{[\hat{x}, \hat{y}, \hat{z}]}$$

It is T^{-1} , the inverse of $T_z(\alpha) T_x(\beta) T_z(\gamma)$.

Thus, $A = (T_z(\alpha) T_x(\beta) T_z(\gamma))^{-1}$ (see footnote¹ below for justification)

$$\begin{aligned}
&= (T_z(\gamma))^{-1} (T_x(\beta))^{-1} (T_z(\alpha))^{-1} \\
&= \begin{pmatrix} \cos \gamma & \sin \gamma & 0 \\ -\sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \beta & \sin \beta \\ 0 & -\sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
&= \begin{pmatrix} \cos \alpha \cos \gamma - \sin \alpha \cos \beta \sin \gamma & \sin \alpha \cos \gamma + \cos \alpha \cos \beta \sin \gamma & \sin \beta \sin \gamma \\ -\cos \alpha \sin \gamma - \sin \alpha \cos \beta \cos \gamma & -\sin \alpha \sin \gamma + \cos \alpha \cos \beta \cos \gamma & \sin \beta \cos \gamma \\ \sin \alpha \sin \beta & -\cos \alpha \sin \beta & \cos \beta \end{pmatrix}
\end{aligned}$$

The inverse of this matrix ($A^{-1} = T$) changes the coordinates of a vector v in the $[\hat{X}, \hat{Y}, \hat{Z}]$ coordinate system to the coordinates of v in the $[\hat{x}, \hat{y}, \hat{z}]$ coordinate system (see eqn. 8).

¹ Given that $T = T_z(\gamma) T_x(\beta) T_z(\alpha)$, so that $T\hat{x} = \hat{X}$, $T\hat{y} = \hat{Y}$, $T\hat{z} = \hat{Z}$, show that $\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = T^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$.

If $X\hat{X} + Y\hat{Y} + Z\hat{Z} = x\hat{x} + y\hat{y} + z\hat{z}$ (i.e., the same vector in two different coordinate systems),

$$\text{then } \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = X\hat{X} + Y\hat{Y} + Z\hat{Z} = XT^{-1}\hat{X} + YT^{-1}\hat{Y} + ZT^{-1}\hat{Z} = T^{-1}(X\hat{X} + Y\hat{Y} + Z\hat{Z}) = T^{-1}(x\hat{x} + y\hat{y} + z\hat{z}) = T^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

B. Fitting Chloroacetone Data

B.1 Results

We used our algorithm to fit the angular distribution measured for the ketene photofragment formed by the photodissociation of chloroacetone to $\text{CH}_3\text{C}(\text{O})\text{CH}_2 + \text{Cl}$ and secondary dissociation of the radical to ketene and methyl. The distribution of relative velocity vectors imparted to the CH_3 and ketene produced in the secondary dissociation was reported in Refs. 1 and 2. Using this and an isotropic secondary angular distribution $I(\theta_{2^\circ})$ gave a good fit to the scattering data using CMLAB2. Thus, we retained this for our fits presented below. The net ketene angular distribution is not isotropic, as the primary C – Cl photofission is not, so we tested our algorithm by using it to fit the $\beta(v_{net})$ output by BASEX.³

We attempted to use the experimental Cl $\beta_{1^\circ}(E_T)$.² One difficulty arose in accounting for the angular distribution of the background in the Cl atom velocity map imaging data taken with REMPI detection. To properly account for the primary Cl photofragment β_{1° , we determined the fraction f of ground state Cl ($^2P_{3/2}$) that was produced by a combination of photodissociation at 193 nm and photoionization at 118 nm by subtracting the background Cl signal produced by 193 nm laser alone. The background Cl signal data is isotropic (shown in Fig. S1) which is represented by $\beta_{\text{background}} = 0$. Using the equation

$$\beta_{\text{measured}} = f\beta_{\text{desired signal}} + (1 - f)\beta_{\text{background}} \quad (1)$$

and that $\beta_{\text{background}} = 0$, we find that

$$\beta_{\text{desired signal}} = \frac{\beta_{\text{measured}}}{f}. \quad (2)$$

We then performed a linear fit of $\beta_{\text{measured}}(E_{1^\circ})$ for Cl, which is shown in Fig. S2. The desired β , shown in Fig. S3, was then obtained by dividing the measured beta in Fig. S2 (which includes a contribution for the background) by the fraction of the signal due to Cl ($^2P_{3/2}$) (Fig. S4).

The $\beta(E_{1^\circ})$ we entered into our program was constant at $\beta = -0.0800$ between 0 and 6.77 kcal/mol (100,000 cm/s), and then follows the data shown in Fig. S3. We only have data with a good signal-to-noise ratio from 6.77 kcal/mol to 21.9 kcal/mol (180,000 cm/s), so we used a sixth order fit ($R^2 = 0.9999$) to match the trend in Fig. S3 from 21.9 kcal/mol (180,000 cm/s) to 26 kcal/mol. Setting $\beta = -0.0800$ from 0 to 6.77 kcal/mol is within the signal-to-noise for energies less than 6.77 kcal/mol (100,000 cm/s). The net fit for this treatment of the primary angular distribution given to the measured ketene angular distribution

data is shown in Fig. S5.

B.2 Discussion

We attempted to fit the dissociation of $\text{CH}_3\text{C}(\text{O})\text{CH}_2 \rightarrow \text{CH}_3 + \text{C}(\text{O})\text{CH}_2$ using the $1/\sin(\theta)$ distribution, but this always resulted in a two-peaked $P(v_{net})$ that does not match our experimental data. Non-coplanar forces in the exit channel likely smeared the $1/\sin(\theta)$ angular distribution.

We considered two possible sources of error to understand why we were unable to obtain a good fit to the measured ketene angular distribution using the experimentally measured anisotropy of the primary C – Cl bond fission from the two step model. We presume the problem arises from the fact that the signal-to-noise ratio for a large portion of the Cl atom data was too low to extract an accurate speed dependent anisotropy parameter to use for the primary dissociation. Subtracting the isotropic background in the anisotropy data is important to do and we give the methodology here, but it introduces a large amount of experimental error because of the poor signal-to-noise ratio.

We also considered the possibility that the Cl signal included a contribution from the dissociation of $\text{C}(\text{O})\text{CH}_2\text{Cl}$ (produced by another primary photofission channel, reaction 1c in Ref. 1) to Cl + ketene. This would contaminate the speed and anisotropy data. As seen in Fig. 2 in Ref. 1, the methyl signal attributed to the dissociation of chloroacetone to $\text{CH}_3 + \text{C}(\text{O})\text{CH}_2\text{Cl}$ has velocities greater than 360,000 cm/s, which corresponds to 27.76 kcal/mol of relative translational energy imparted to the primary photofragments. Using conservation of energy

$$E_{int,\text{C}(\text{O})\text{CH}_2\text{Cl}} = h\nu + E_{int,\text{chloroacetone}} - D_0(\text{C} - \text{Cl}) - E_{int,\text{CH}_3} - E_T \quad (3)$$

and assuming the methyl product does not carry away any internal energy, we can calculate the internal energy of $\text{C}(\text{O})\text{CH}_2\text{Cl}$ radicals that correspond to the slowest methyl produced by this channel. At 193.3 nm, $h\nu = 147.8\text{kcal/mol}$, $E_{int,\text{chloroacetone}}$ at the nozzle temperature of 80°C is 4.8 kcal/mol, and $D_0(\text{C} - \text{Cl})$ is 82.2 kcal/mol at the G3/B3LYP level of theory.¹ The endoergicity of the dissociation of $\text{C}(\text{O})\text{CH}_2\text{Cl} \rightarrow \text{C}(\text{O})\text{CH}_2 + \text{Cl}$ is 21.68 kcal/mol, calculated at the G4//B3LYP/6-311++G(3df,2p) level of theory. Thus, this dissociation is allowed because there is 20.96 kcal/mol of internal energy in $\text{C}(\text{O})\text{CH}_2\text{Cl}$ above the endoergicity if methyl is given a speed of 360,000 cm/s. This channel is therefore a potential source of ketene and Cl atoms, but since the secondary dissociation has no barrier beyond the endoergicity, we assume that little to no additional velocity should be imparted to Cl + ketene. This allows us to predict

the speed of the resulting Cl and ketene cofragments. Since all methyl produced by the primary photodissociation channel have velocities between 360,000 cm/s and 440,000 cm/s, the Cl or ketene signal produced in secondary dissociation would be found between 70,000-86,000 cm/s. These speeds were not in the range of Cl atom speeds used to determine the experimental $\beta(v_{1^0})$ for Cl, so this did not affect our analysis. Additionally, the dissociation of $\text{C}(\text{O})\text{CH}_2\text{Cl} \rightarrow \text{CO} + \text{CH}_2\text{Cl}$ has a lower barrier height, 18.60 kcal/mol, and is endoergic by only 3.92 kcal/mol as calculated at the G4//B3LYP/6-311++G(3df,2p) level of theory, so we expect any unstable $\text{C}(\text{O})\text{CH}_2\text{Cl}$ photofragment to dissociate to $\text{CO} + \text{CH}_2\text{Cl}$ rather than to Cl + ketene.

References

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- [2] Alligood, B. W.; FitzPatrick, B. L.; Szpunar, D. E.; Butler, L. J. *J. Chem. Phys.* **2011**, *134*, 054301.
- [3] Dribinski, V.; Ossadtchi, A.; Mandelshtam, V. A.; Reisler, H. *Rev. Sci. Instrum.* **2002**, *73*, 2634–2642.

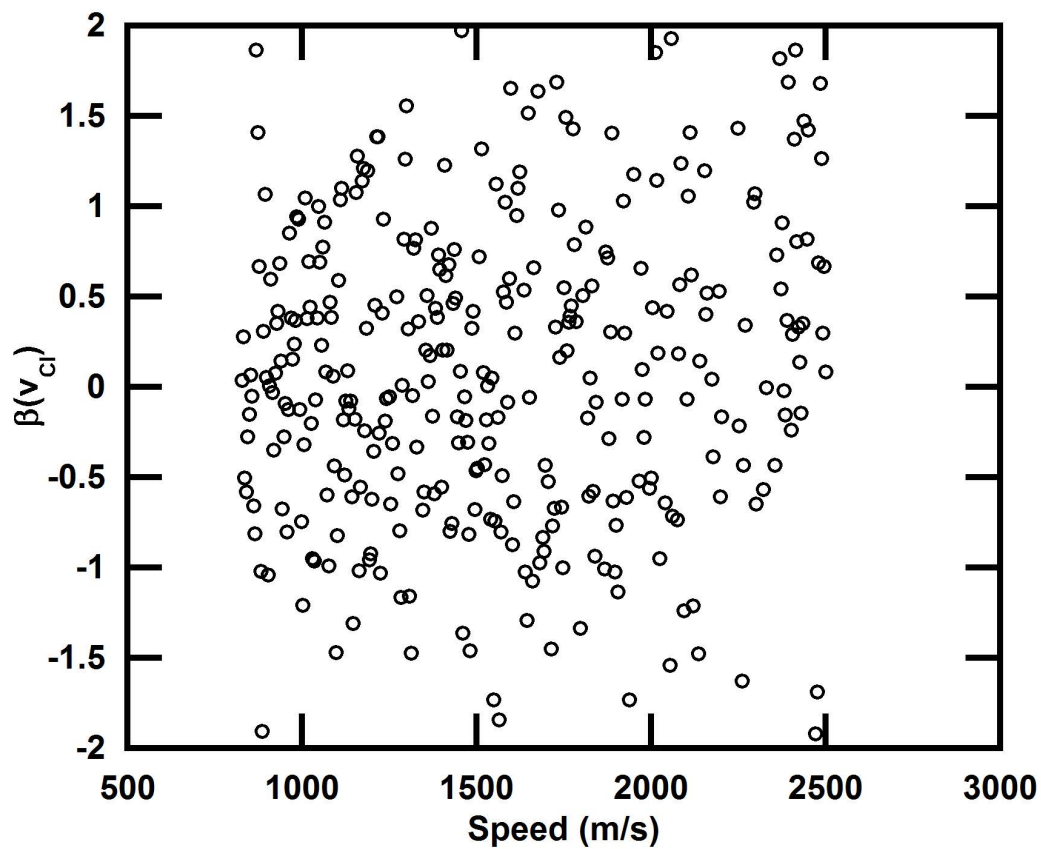


Figure S1: Anisotropy data for background at $m/e = 35$ taken with 193 nm light only, which was first reported in Ref. 2. It is isotropic.

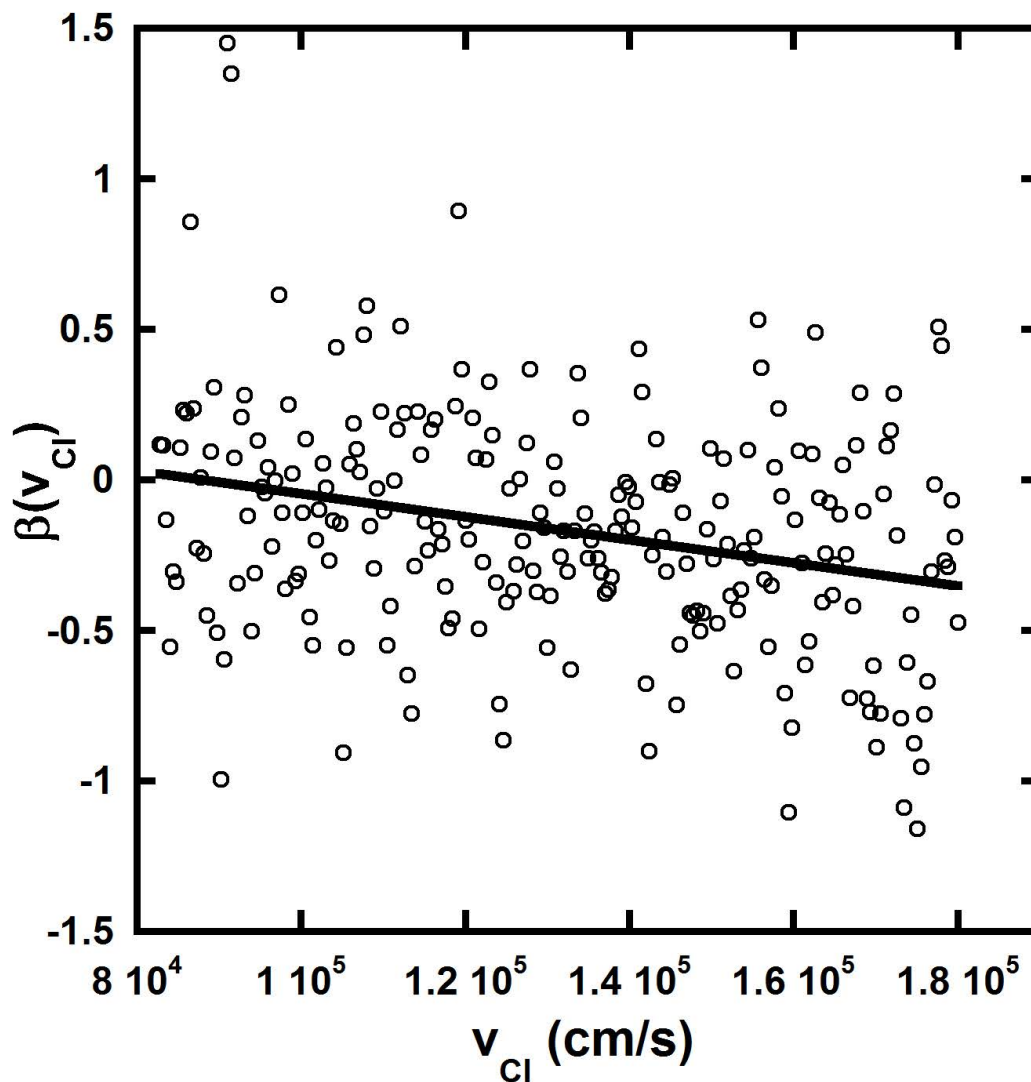


Figure S2: The speed dependence of the anisotropy parameter measured for the total signal (Cl ($^2P_{3/2}$) and background) at $m/e = 35$. The data in open circles was reported in the supplemental documents of Ref. 2. The linear fit shown in black has the equation $\beta(v_{Cl}) = 3.83 \times 10^{-6}v + 0.339$. This fit is subsequently corrected (see Fig. S3) for the background contribution from the 193 nm data only (no REMPI laser; shown in Fig. S4).

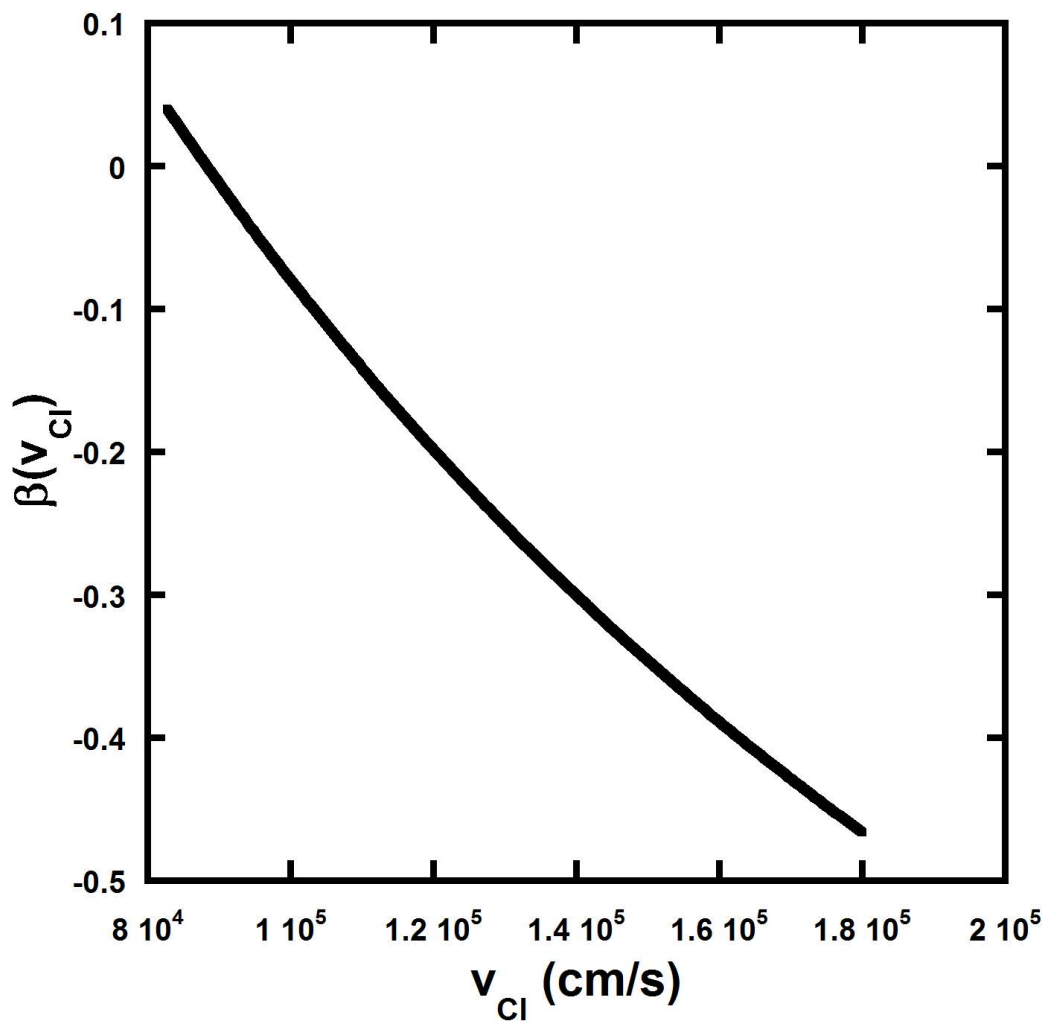


Figure S3: The corrected experimental $\beta(v)$ for Cl ($^2P_{3/2}$), obtained by dividing by the linear fit shown in Fig. S2 by the fraction of signal from Cl ($^2P_{3/2}$) photofragments detected with REMPI. This corrects the measured $\beta(v_{Cl})$ presented in Fig. S2 for the contribution from an isotropic background from the 193 nm laser only.

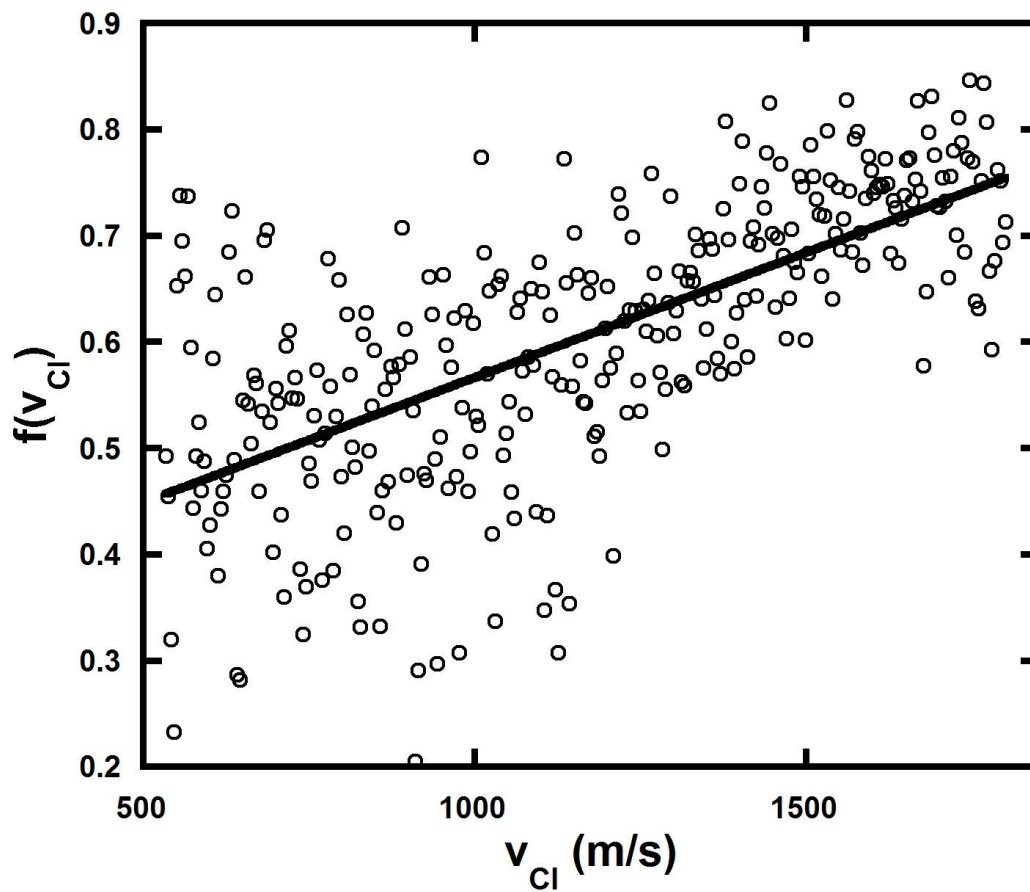


Figure S4: The fraction $f(v_{Cl})$ of ground state Cl ($^2P_{3/2}$) that is produced by photodissociation at 193 nm and detected with REMPI. The linear fit is shown in black and has the equation $\beta(v) = 2.35 \times 10^{-4}v + 0.331$ (in m/s).

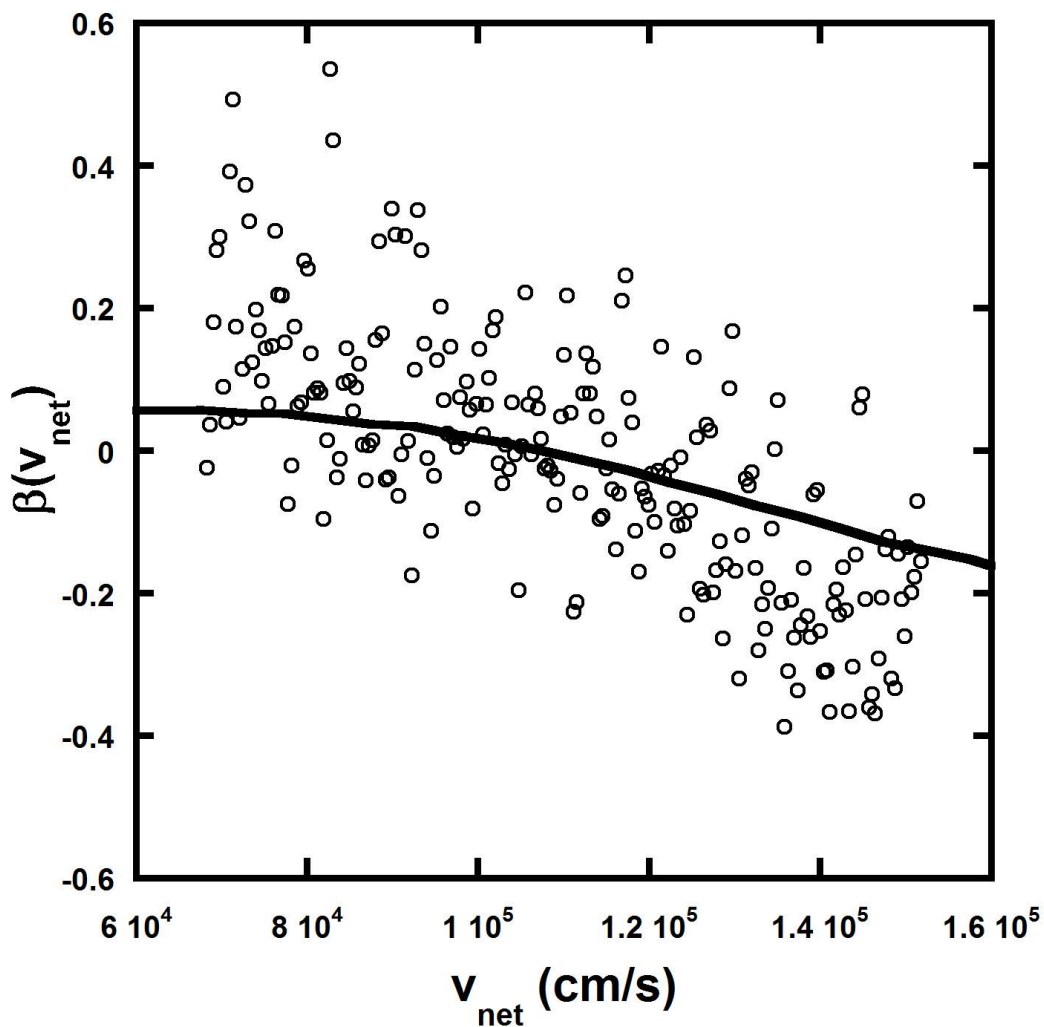


Figure S5: The angular distribution of the ketene secondary product from chloroacetone at 193 nm. Data from Ref. 2 is shown in open circles. The fit shown in solid line is calculated by the two-step algorithm presented herein. This fit uses the background corrected experimental $\beta(v_{\text{Cl}})$ shown in Fig. S3 and described in the text. The other input parameters used to calculate the fit were the portion of the primary C – Cl photofission $P(E_T)$ that generate unstable radicals (Ref. 2, Fig. 5), the secondary $P(E_T)$ given in Ref. 2, Fig. 12, and an isotropic secondary angular distribution. The net speed distribution of the ketene is well fit in Fig. 1 of Ref. 1. The fit shown in this figure is the best fit we can obtain from the experimental Cl atom data.