Use of the spatial phase of a focused laser beam to yield mechanistic information about photo-induced chemical reactions

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Abstract. Two-pathway quantum mechanical interference was used to control the photoionization and photodissociation of a number of polyatomic molecules. The phase lag between different pairs of products obtained from acetone and dimethyl sulfide was altered by translating the focus of the laser beam along an axis normal to the molecular beam axis. This effect was derived quantitatively from the spatial Gouy phase of the laser beam. Details of the chemical reaction mechanisms were deduced from the channel phase lags, obtained when the laser was focused on the axis of the molecular beam, and from the variation of the phase lag produced by axial translation of the laser focus.
1. Introduction

In conventional photochemical reactions, the phase of the radiation field does not play a role in the reaction mechanism. It has been known for some time, however, that if two coherent light sources are used to initiate competing reaction paths, quantum interference between those paths can alter the yield and product branching ratio \[^{[1]}\]. By varying the relative phase of a bichromatic field, it is possible to modulate the product yield, in analogy to Young’s two-slit experiment. The appearance of a phase lag between different pairs of products is the hallmark of coherent control \[^{[2]}\].

In typical two-path quantum control experiments, all the products are formed at the same total energy. In such a situation, relatively little dynamical information is learned from the phase lag. In a recent series of papers, however, we showed that if formation of some of the products requires the absorption of additional photons after the control step, it is possible to extract information from the phase lag about the reaction paths leading to those products \[^{[3]}–^[5]}\]. Consider the case of bichromatic excitation by \(n\) photons of frequency \(\omega_m\) and \(m\) photons of frequency \(\omega_n\), such that \(n\omega_m = m\omega_n\). The spatially-dependent phase of the \(\omega_n\) electric field is given by

\[
\phi_{sp,\omega_n}(z) = \phi_n + k_n z - \tan^{-1}(z/z_R),
\]

where \(z\) is the axial distance from the focal point of the laser, \(z_R\) is its Rayleigh range, \(\phi_n\) is the constant part of the phase, and \(k_n\) is the wavenumber. The third term on the right-hand side, known as the Gouy phase, increases by \(\pi\) as the electromagnetic wave passes through a focus \[^{[6]}\]. The overall phase for bichromatic excitation is given by

\[
\phi_{sp}(z) = (m\phi_n - n\phi_m) + (mk_n - nk_m) z + (n - m) \tan^{-1}(z/z_R).
\]

This phase appears in the probability of obtaining product \(S\),

\[
P^S = P^S_m + P^S_n + P^S_{mn} \cos(\phi_{sp} - \delta^S_{mn}),
\]

where \(P^S_m\) and \(P^S_n\) are the reaction probabilities for the individual fields, \(P^S_{mn}\) is the amplitude of the cross-term, and \(\delta^S_{mn}\) is the molecular phase associated with that channel \[^{[5]}\]. The branching ratio may be controlled by varying \(\phi_{sp}\), so that the yield of channel \(S\) is maximized when \(\phi_{sp} = \delta^S_{mn}\). Usually \(\phi_{sp}\) is varied by adjusting the first term on the right-hand side of equation (2).
This is typically accomplished by passing both beams through a medium of variable optical density and taking advantage of the wavelength dependence of the refractive index of the medium. The second term usually vanishes because of conservation of linear momentum. The third term, the Gouy phase shift, also vanishes if the products are formed at the same energy, because $n - m$ is the same for all channels. As explained below, however, the Gouy phase shift need not cancel out if one of the products requires the absorption of additional photons following the control step. We designate the number of additional photons required by the integer $l$.

Chen and Elliot [7] demonstrated that the modulation of the signal produced by one- and three-photon ionization of mercury atoms undergoes a Gouy phase shift as the probed region passes through the focal point of the laser beams. This effect in itself is insufficient to affect the branching ratio of a chemical reaction because the phase contribution of the $l$ additional photons to the two interfering paths cancels exactly, and the contribution of the $(n - m) \tan^{-1}(z/z_R)$ term at any given point in space is equal for all channels. The effect of the additional photons in some particular channel is to confine the products to a smaller volume, so that a spatial average of the product yield may have a channel-dependent contribution from the Gouy phase. This effect averages to zero if the laser is focused onto the axis of the molecular beam, because the Gouy phase is an antisymmetric function of $z$. If the laser is focused off axis, however, the spatial symmetry of the products is broken, and a spatial average of the yield contains a nonzero Gouy phase contribution.

In a recent study [3], we demonstrated a Gouy phase contribution to the branching ratio of the photoionization versus photodissociation of vinyl chloride (CH$_2$CHCl, VCl) in three- versus one-photon excitation at 532 and 177 nm. Phase control of the reaction products for this molecule is of interest because it shows that the high density of states of a multicenter polyatomic molecule need not destroy the coherence effects that were previously observed for simpler molecules. From the Gouy effect we determined that breaking of the C–Cl bond in VCl occurs by fragmentation of the neutral molecule at the $3\omega_1$ level rather than by fragmentation of the VCl$^+$ ion at the $5\omega_1$ level. Moreover, we found that the axial dependence of the phase lag is in quantitative agreement with the calculated value for $l = 2$, $m = 3$, and $n = 1$ without any adjustable parameters.

Here we extend our studies to additional polyatomic molecules in order to test our understanding of the effect of the Gouy phase. Acetone (CH$_3$COCH$_3$), like VCl, requires three 532 nm photons to fragment and five photons to ionize (i.e. $l = 2$). The density of states of acetone is much greater, however, because of the presence of four heavy atoms. Dimethyl sulfide (DMS, CH$_3$SCH$_3$) provides an interesting contrast to both molecules because it requires only one excess photon ($l = 1$, IP = 8.69 eV [8]) to ionize. This molecule is of interest also because its control was investigated previously by Nagai et al [9] at a lower photon energy, although without consideration of the Gouy effect. Last, we briefly investigate the phase response of a number of other polyatomic compounds to see how general is the controllability of complex molecules.

2. Experimental

The experimental setup was described previously [3]. Briefly, a pulsed molecular beam of the neat sample gas was simultaneously excited with 532 and 177 nm radiation. The 532 nm light was the output of a 4 ns, frequency doubled Nd:YAG laser, whereas the 177 nm was obtained by frequency tripling the 532 nm radiation in a Hg oven. The energy of the 532 nm laser was
Figure 1. The 532 nm mass spectrum of acetone.

24–29 mJ pulse$^{-1}$. The temperature of the Hg oven was typically 119–121 °C in the vicinity of the laser focus.

The molecular and laser beams intersected at 90°. The coaxial laser beams were focused onto the target by a pair of UV-coated spherical mirrors, one concave and one convex. The off-axis configuration of the mirrors produces two astigmatic, elliptical foci, one perpendicular to the plane defined by the laser and molecular beam axes and the other in the plane of intersection. All the data reported here used the in-plane focus, where the intensity was approximately $1 \times 10^{13}$ W cm$^{-2}$. The mirrors were mounted in a cell containing hydrogen gas, which was used to control the relative phase of the laser beams. The reaction products were detected with a home-built time-of-flight mass spectrometer.

The molecular beam had a Gaussian profile with a full width at half maximum of 397 µm at the intersection point. This quantity was determined by deconvoluting the profile measured by scanning one of the focusing mirrors along a direction perpendicular to the molecular beam axis. In the Gouy phase experiment, this scan was repeated ten times to determine the precise location and standard deviation of the peak maximum. This peak location defines the origin of the z-axis used in equation (2) to define the Gouy phase. Next, the ion yield versus $H_2$ pressure in the tuning cell was measured for the fragment ions of interest at different positions of the laser focus, with the axis of the molecular beam located at a distance $z_m$ from the focal line.

DMS (>99% purity), 1,1-dichloroethylene (99%), iodobenzene (98%) and toluene (>99.5%) were obtained from Sigma-Aldrich Inc., and acetone (Certified ACS Spectranalyzed) was obtained from Fisher Scientific.

3. Results

Figure 1 shows the mass spectrum of acetone obtained with just the 532 nm laser. The mass spectrum is dominated by three peaks corresponding to CH$_3^+$, CH$_3$CO$^+$ and CH$_3$COCH$_3^+$. Strong modulations were observed for all three ions and are shown in figure 2. At $z_m = 0$, a phase lag of $\Delta\delta$(CH$_3$COCH$_3^+$, CH$_3$CO$^+$) = 6.3 ± 4.0° was measured, with CH$_3$COCH$_3^+$ leading CH$_3$CO$^+$. The phase lag between CH$_3^+$ and CH$_3$CO$^+$ is 0.2 ± 5.6°. Another experiment was performed with acetone mixed with VCl, and the modulations in CH$_3$CO$^+$, CH$_3$COCH$_3^+$ and VCl$^+$ were recorded.
simultaneously. The phase lag between CH$_3$COCH$_3^+$ and VCl$^+$ is not significantly different from zero. The modulation depths for CH$_3$CO$^+$, CH$_3^+$, CH$_3$COCH$_3^+$ and VCl$^+$ are 14, 25, 35 and 28%, respectively. We note that the acetyl peak is the most intense in the mass spectrum but has the smallest modulation depth. The phase lag between the acetyl and acetone ions obtained at five values of $z_m$ (the ‘Gouy profile’) is plotted in figure 3. Also shown in this figure is the previously published [3] Gouy profile for VCl, which is seen to be very similar to that of acetone.

The mass spectrum for DMS is shown in figure 4. The 532 nm photoionization spectrum includes all the peaks observed previously by Nagai et al [9] at 602.5 nm, but much greater fragmentation is evident. The parent ion is just barely visible, and its phase modulation was too weak for quantitative study. Peaks that showed strong modulation are CH$_3^+$, SCH$_3^+$ and
Figure 3. The phase lag as a function of the distance of the molecular beam axis from the focal line of the laser. A positive phase lag corresponds to a parent ion signal ($\text{VCl}^+$ or $\text{CH}_3\text{COCH}_3^+$) leading the fragment ($\text{C}_2\text{H}_5^+$ or $\text{CH}_3\text{CO}^+$). The vinyl chloride data are taken from [3]. The solid curve is the numerical calculation of the spatial phase lag using the methods described in [4], taking into account the astigmatic focus of the laser beam and the Gaussian profile of the molecular beam.

Figure 4. Time-of-flight mass spectrum of DMS obtained at 532 nm. Only the products with the $^{32}\text{S}$ isotopomer are labeled.

$\text{CH}_3\text{SCH}_2^+$, which are produced by scission of the S–C and S–H bonds. The modulation curves for these products at $z_m = 0$ are plotted in figure 5, displaying modulation depths of 9, 6 and 6%, respectively. Values of the phase lags measured at different $z_m$ are listed in table 1. The variation between runs on different days was much larger than has been observed for other molecules, but the slopes of the phase lag versus $z_m$ were reproducible. In the subsequent analysis we use the first line of each data set in the table, which contains five values of $z_m$. These Gouy profiles are shown in figure 6.
We also measured the phase modulation between fragmentation channels of 1,1-dichloroethylene (CH$_2$=CCl$_2$, DCE) at $z_m = 0$. Figure 7 shows the time-of-flight mass spectrum obtained with just the 532 nm beam. Notably absent in the mass spectrum is the parent ion. Figure 8 shows strong modulation of the C$_2$H$_2$, C$_2$HCl and Cl fragments. No phase lag was observed between any of the products at $z_m = 0$. No modulation was found for trimethyl amine, iodobenzene and toluene.
Table 1. Phase lag values for the fragments and parent ion of DMS obtained at various positions of the laser focus within the molecular beam profile.

| $z_m (\mu m)$ | $\Delta \delta$ (degrees) | Slope |
|---------------|---------------------------|-------|
|               | -331.2                    | 0     | +220.8 | +331.2 |
| SC$_2$H$_5^+$ - CH$_3^+$ | 78 ± 3.5 | 37 ± 2.7 | 0.8 ± 2.5 | -19 ± 3.5 | -0.15 ± 0.01 |
|               | 86 ± 3.4 | 17 ± 3.4 | -42 ± 3.4 | -0.19 ± 0.01 |
| SC$_2$H$_5^+$ - SCH$_3^+$ | 27 ± 2.7 | 23 ± 2.4 | 6.5 ± 2.7 | -4.2 ± 2.7 | -17 ± 3.4 | -0.06 ± 0.01 |
|               | 33 ± 3 | 3.5 ± 3.2 | -23 ± 2.7 | -0.08 ± 0.01 |
|               | 14 ± 2.4 | 2.1 ± 3 | -19 ± 4 | -0.05 ± 0.01 |
| SCH$_3^+$ - CH$_3^+$ | 51 ± 3.6 | 49 ± 3 | 30 ± 2.7 | 5 ± 2.4 | -2 ± 3.2 | -0.09 ± 0.01 |
|               | 52 ± 3.7 | 21 ± 3.6 | -18 ± 3.4 | -0.10 ± 0.01 |
|               | 39 ± 3 | 12 ± 3 | -20 ± 3.7 | -0.09 ± 0.01 |

Figure 6. Gouy phase shifts for various pairs of fragment ions measured in the coherent control of dimethyl sulfide. The dashed, solid and dash-dotted lines were calculated for an astigmatic focus using a Gaussian molecular beam profile, with $m = 1$ and $n = 3$. The dashed curve corresponds to $l = 0$ for one channel and $l = 3$ for the second channel, the solid curve corresponds to $l = 0$ for one channel and $l = 2$ for the second channel, and the dash-dotted curve corresponds to $l = 2$ for one channel and $l = 3$ for the second channel. A phase lag of $39^\circ$, $26^\circ$ and $6^\circ$ was added to the dashed, solid and the dash-dotted curves, respectively, to bring them into agreement with the channel phase lags measured at $z_m = 0$.

4. Discussion

4.1. Acetone

Photodissociation of acetone is a classic Norrish-type I reaction resulting from $\alpha$-cleavage of a carbon–carbon bond. The three lowest-energy pathways are accessed by $S_1 \leftarrow S_0(\pi^* \leftarrow n)$, $S_2 \leftarrow S_0(3s \leftarrow n)$ and $S_3 \leftarrow S_0(4s \leftarrow n)$ transitions, involving non-bonding (n), anti-bonding
Figure 7. Time-of-flight mass spectrum of 1,1-dichloroethylene. The unlabeled peaks are $^{37}\text{Cl}$ isotopomers. The NO$^+$ and C$_2$H$_3^+$ peaks are from NO and vinyl chloride impurities sticking in the sample line.

($\pi^*$), and Rydberg ($ns$) orbitals [10]. The experimental onset of the $\pi^* \leftarrow n$ transition occurs at 3.75 eV, with a maximum at 4.38 eV. The threshold shifts down to 3.56 eV when singlet–triplet mixing is taken into account [11]. The vertical energies for transitions to the Rydberg states are 6.35 eV for $n = 3$ and 8.46 eV for $n = 4$ [12]. The ionization potential of acetone is 9.70 eV [8].

In the lowest energy ($n, \pi^*$) channel, acetone predissociates into CH$_3$CO and CH$_3$ radicals. An early study of the S$_2$ channel indicated that at 193 nm the molecule dissociates synchronously into three fragments, CH$_3$ + CO + CH$_3$ [13]. Later studies, however, showed that the reaction proceeds through a stepwise mechanism [10, 14]. The acetyl radical forms in about 50 fs and then decomposes into CO + CH$_3$ fragments, with the lifetime of the radical intermediate decreasing with increasing excitation energy.

Three distinct mechanisms for the formation of the acetyl cation (CH$_3$CO$^+$) are possible: (i) dissociative ionization of neutral acetone, (ii) photodissociation of acetone ions and (iii) photoionization of neutral acetyl radicals. The threshold for pathway (i), measured by photoionization with a single VUV photon, was reported to be 10.38 eV [15]. Mechanism (ii) was studied by photofragment imaging using one 118 nm photon to produce the acetone cation and two 355 nm photons to dissociate the ion via a metastable state [16]. The data revealed that acetyl cations and methyl radicals are the primary products. Competition between paths (ii) and (iii) was observed using sub-ps 585 nm radiation [17].

A mechanism that is consistent with the previous experiments and our current results consists of the following elementary reactions:

\[
\begin{align*}
\text{CH$_3$COCH$_3$(S$_0$)} + 2\omega_1 & \rightarrow \text{CH$_3$COCH$_3$(S$_1$)} \quad (R1) \\
\text{CH$_3$COCH$_3$(S$_1$)} & \rightarrow \text{CH$_3$CO} + \text{CH}_3 \quad (R2) \\
\text{CH$_3$COCH$_3$(S$_0$)} + 3\omega_1, \omega_3 & \rightarrow \text{CH$_3$COCH$_3$(S$_2$)} \quad (R3) \\
\text{CH$_3$COCH$_3$(S$_2$)} & \rightarrow \text{CH$_3$CO}^* + \text{CH}_3 \quad (R4) \\
\text{CH$_3$CO}^* & \rightarrow \text{CH}_3 + \text{CO} \quad (R5)
\end{align*}
\]
Figure 8. Modulation curves of various fragments of 1,1-dichloroethylene.

\[
\begin{align*}
\text{(a) C}_2\text{H}_2^+ \\
\text{CH}_3\text{COCH}_3(S_0) + \{5\omega_1, \omega_3 + 2\omega_1\} & \rightarrow \text{CH}_3\text{COCH}_3^+ + e^- & \text{(R6)} \\
\text{CH}_3\text{COCH}_3^+ & \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3 \\
\text{(b) C}_2\text{HCl}^+ \\
\text{CH}_3\text{COCH}_3(S_0) + \{5\omega_1, \omega_3 + 2\omega_1\} & \rightarrow \text{CH}_3\text{COCH}_3^+ + e^- & \text{(R6)} \\
\text{CH}_3\text{COCH}_3^+ & \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3 \\
\text{(c) Cl}^+ \\
\text{CH}_3\text{COCH}_3(S_0) + \{5\omega_1, \omega_3 + 2\omega_1\} & \rightarrow \text{CH}_3\text{COCH}_3^+ + e^- & \text{(R6)} \\
\text{CH}_3\text{COCH}_3^+ & \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3 \\
\end{align*}
\]

Neutral methyl radicals produced in reactions \((\text{R2})\), \((\text{R4})\) and \((\text{R7})\) may absorb additional photons to yield \(\text{CH}_3^+\) ions. Similarly, metastable \(\text{CH}_3\text{CO}^+\) produced in reaction \((\text{R4})\) may survive long enough to be photoionized. The strong acetyl peak in figure 1 is expected because of the multiple paths for its formation discussed above. The much lower ionization potential of acetyl \([18]\) versus methyl \([19]\) radicals (7.01 versus 9.84 eV) helps to explain the greater relative intensity of the acetyl peak. The preponderance of acetyl versus methyl ions in the mass spectrum could also be explained by the selectivity of reaction \((\text{R7})\) \([17]\), but we will argue later that this reaction is negligible under our conditions.

Our phase modulation data may be understood in terms of this mechanism. Consider first the data at \(z_m = 0\). Modulation of the acetyl and parent ion signals results from two-pathway interference in both reactions \((\text{R3})\) and \((\text{R6})\). The zero phase lag between \(\text{CH}_3\text{CO}\) and \(\text{CH}_3\)
is consistent with their originating from the same precursor in reaction (R4). The very small phase lag between the acetyl and parent ions, if real, could be due to the channel phase that results from coupling of the 3s Rydberg bound state to an antibonding state [20]. The smaller modulation depths of the acetyl and methyl products might be explained by a large two-photon contribution from reactions (R1) and (R2), for which there is no coherently competing path.

We turn now to the effect of the Gouy phase. The curve in figure 3 was calculated by averaging equation (3) over the radial and axial coordinates of the laser beam, as described previously [4], taking into account the astigmatic focus of the laser and the Gaussian profile of the molecular beam. The calculation was performed assuming interference between the $\omega_3$ and $3\omega_1$ paths in the dissociation channel and between the $\omega_3 + 2\omega_1$ and $5\omega_1$ paths in the ionization channel. Good agreement is obtained between the data and the theory. From our results we infer that acetone dissociates by absorbing either one photon of 177 nm radiation or three photons of 532 nm radiation, to yield the neutral products in reactions (R3)–(R5). The molecule may absorb two additional 532 nm photons to produce the parent ion in (R6). Dissociative ionization (R7) does not appear to play a significant role, because there is no Gouy phase lag between the acetyl ion produced in this channel and the parent ion, contrary to the data in figure 3.

### 4.2. DMS

The photodissociation dynamics of DMS has been studied extensively in the near UV [21], ([22] and references cited therein). The primary excitation step for wavelengths $>190$ nm is the promotion of a non-bonding sulfur electron (from $3b_1$, the highest occupied molecular orbital) to a 4s Rydberg-like orbital ($9a_1$) or a valence-like C–S anti-bonding ($6b_1$) orbital [23, 24]. Only the $X^1A_1 \rightarrow 1^1B_1$ transition is dipole allowed. The vibronic coupling, however, mixes the $1^1A_1$ and $1^1B_1$ states, which cross at a conical intersection to become the $1^1A''$ and $2^1A''$ states. Dissociation on the $1^1A''$ surface yields SCH$_3$ + CH$_3$. At the shorter wavelength used in the present study (177 nm, corresponding to $\omega_3$), higher-energy Rydberg orbitals, such as the $5s(a_1)$, $4p(b_1)$, $3d(a_1)$ and $3d(b_1)$, are populated [25], and presumably higher lying conical intersections involving the C–S reaction coordinate provide efficient paths to form the same products. As shown in figure 9, electronically excited SCH$_3$ can also be formed at this energy. Another reaction channel yields the products CH$_3$SCH$_2$ + H [26]. The pathway for this reaction presumably involves a different set of conical intersections along the C–H stretch coordinate. We shall argue later, however, that under our experimental conditions the CH$_3$SCH$_2^+$ ion is formed primarily by dissociative ionization.

In our experiment, the parent ion is barely visible, whereas the primary fragment ions, CH$_3$SCH$_2^+$, SCH$_3^+$ and CH$_3^+$ are present with comparable intensities (figure 4), and all show strong phase modulation. We consider first the channel phase lags for pairs of these products, measured at $\tilde{z}_m = 0$. The 30° phase lag between SCH$_3^+$ and CH$_3^+$ proves that these fragments must come from different reaction channels (see footnote 4). We assign the CH$_3^+$ signal to the three-photon ($3\omega_1$) dissociation of DMS (subsequently ionized by five additional $\omega_1$ photons), and SCH$_3^+$ to 5$\omega_1$ coherent dissociative ionization of DMS. A possible source of the channel phase is the vibronic coupling of the bound and continuum states at the conical intersection that leads to neutral SCH$_3$ and CH$_3$. As we propose in the following paragraph, an elastic dissociative ionization.

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4 A zero phase lag is a necessary but not a sufficient condition for two products to be formed from a single precursor.
The ionization continuum has a channel phase of zero and therefore does not contribute to the phase lag [27].

The 37° channel phase lag between CH₃SCH₂⁺ and CH⁺₃ likewise shows that these products come from different pathways, with CH₃SCH⁺₂ again the product of coherent dissociative ionization. The small, possibly zero, phase lag between CH₃SCH⁺₂ and SCH⁺₃ at zm = 0 is consistent with both products coming from elastic dissociative ionization.

More information about the reaction mechanism may be obtained from the Gouy profiles. In particular, we find that the slopes of these profiles support the assignments made in the previous two paragraphs. Figure 6 shows that the slope of ∆δ(CH₃SCH⁺₂, CH⁺₃) versus zm is greater than the slope of ∆δ(SCH⁺₃, CH⁺₃), which is in turn greater than the slope of ∆δ(CH₂SCH⁺₂, SCH⁺₃). The solid curve, calculated assuming that l = 2 for SCH⁺₃ and l = 0 for CH⁺₃, is in fair agreement with the data and supports the mechanism proposed above. That is, SCH⁺₃ is produced at the five-photon level and CH⁺₃ is produced at the three-photon level. The question arises what happens to SCH⁺₃ produced at the three-photon level. Nourbakhsh et al [26] reported the secondary dissociation of the neutral SCH₃ fragment at 193 nm. The potential energy of the SCH₃ radical along the C–S reaction coordinate [16] shows a A⁺²A₁ bound state coupled to a B⁻²A₁ repulsive state, which can be accessed by two photons of 532 nm. We propose that here the neutral SCH₃ fragment undergoes a rapid secondary dissociation by absorbing two 532 nm photons, and hence has a smaller contribution to the peak observed in the mass spectrum. The S⁺ observed in our 532 nm photoionization mass spectrum of DMS (figure 6) supports this argument.

From the above discussion we conclude that SCH⁺₃ and CH⁺₃ are produced in different reactions: SCH⁺₃ is produced by five-photon dissociative ionization of DMS and neutral CH⁺₃ by three-photon dissociation of DMS. (Although an additional five photons are required to ionize CH⁺₃, they do not contribute to the phase lag [3]). The ionization potential of DMS is 8.69 eV [8], which corresponds to four 532 nm photons. Nourbakhsh et al [26] reported an
appearance energy of 10.67 eV for SCH$_3^+$. This finding supports the assignment of SCH$_3^+$ to dissociative ionization. The methyl fragment produced from the dissociative ionization of the parent ion could also contribute to the methyl peak observed in the mass spectrum. The phase lag data indicate, however, that the contribution of neutral methyl fragments from this channel is negligible. That is to say that the relative number density of the methyl fragments produced by dissociative ionization is much smaller than that of the neutral methyl fragments produced at the three-photon level.

Let us look now at the CH$_3$SCH$_2^+$ product. Figure 6 displays a spatial phase lag between CH$_3$SCH$_2^+$ and SCH$_3^+$, which indicates that CH$_3$SCH$_2^+$ is produced at a higher energy than SCH$_3^+$. A possible explanation is that a vertical transition producing CH$_3$SCH$_2^+$ by dissociative ionization requires the absorption of an additional $\omega_1$ photon. The dash-dotted line in figure 6 corresponds to $l = 2$ for the SCH$_3^+$ channel and $l = 3$ for the CH$_3$SCH$_2^+$ channel. The higher experimental phase lag obtained for CH$_3$SCH$_2^+$ and SCH$_3^+$ as compared to the calculated dash-dotted line suggests the possibility that some fraction of SCH$_3^+$ formed at the three-photon level also contributes to this phase lag. If this explanation is correct, the SCH$_3^+$ and CH$_3^+$ phase lag profile should lie slightly below the solid curve.

Our observations are consistent with the following control mechanism for DMS:

\[
\begin{align*}
\text{CH}_3\text{SCH}_3 + \omega_3, 3\omega_1 & \rightarrow \text{CH}_3\text{SCH}_2^+ \\
\text{CH}_3\text{SCH}_2^+ & \rightarrow \text{SCH}_3 + \text{CH}_3 \\
\text{CH}_3\text{SCH}_3 + \{5\omega_1, \omega_3 + 2\omega_1\} & \rightarrow \text{SCH}_3^+ + \text{CH}_3 + e^- \\
\text{CH}_3\text{SCH}_3 + \{6\omega_1, \omega_3 + 3\omega_1\} & \rightarrow \text{CH}_3\text{SCH}_2^+ + \text{H} + e^-
\end{align*}
\]

The energetics of this mechanism are depicted in figure 9. This scheme is necessarily an oversimplification. It is unlikely, for example, that all of the SCH$_3$ produced in (R9) is dissociated and that none of the CH$_3$ produced in (R10) contributes to the phase lags. Also, it is likely that some parent ions produced by $4\omega_1, \omega_3 + \omega_1$ interference are dissociated incoherently by the absorption of one more $\omega_1$ photon and contribute to the observed phase lags of the fragments. Nevertheless, this mechanism accounts qualitatively for the observed channel phase lags and for the slopes of the three Gouy profiles. We note a third pathway produced by the absorption of $2\omega_3$ photons is possible in (R11), but there is no evidence for it in the sinusoidal modulation curves. We also note that $2\omega_3$ excitation could produce all three products without quantum interference. This incoherent pathway could explain the small modulation depths in figure 5.

The present study complements the earlier work of Nagai et al [9], who measured the phase lag between CH$_3$SCH$_2^+$ and SCH$_3^+$ at fundamental wavelengths between 600.0 and 602.5 nm. A maximum phase lag of $8^\circ$ was observed at 601.5 nm. The falloff of the phase lag at longer and shorter wavelengths could be explained by a three-photon resonance embedded in the dissociative continuum of one of the product channels [27]. The CH$_3$SCH$_2^+$ signal was attributed to H atom ejection following $\omega_3, 3\omega_1$ excitation, rather than the dissociative ionization mechanism proposed here. The two mechanisms are not necessarily inconsistent, considering that different electronic states of DMS are accessed in the two experiments. It would be interesting to test the mechanism at the longer wavelengths by measuring the Gouy phase lag.
4.3. Other molecules

Of the various other large molecules that we studied, 1,1-dichloroethylene is the only one that showed phase modulation. The photochemistry of this molecule is complex because of its many competing reaction channels, including H and Cl ejection and H₂ and HCl elimination [28]. The strong modulation of the three observed fragments demonstrates that two-pathway control is possible even in such complex systems. Gouy phase measurements were not performed, and without such data it is difficult to draw any mechanistic inferences.

The other molecules we studied, trimethyl amine, iodobenzene and toluene, did not display any modulation. The absence of modulation in these molecules may be explained by the following analysis. The modulation depth, \( M \), is given by

\[
M = \frac{P_m^S}{P_m^S + P_n^S} = \frac{2\langle fg \rangle}{\langle f^2 \rangle + \langle g^2 \rangle},
\]

where

\[
\langle f^2 \rangle = \int \langle X | D^{(m)} | ES\hat{k}^- \rangle \langle ES\hat{k}^- | D^{(m)} | X \rangle d^2\hat{k},
\]

with an equivalent expression for \( \langle g^2 \rangle \) using \( D^{(n)} \), and

\[
\langle fg \rangle = \int \langle X | D^{(m)} | ES\hat{k}^- \rangle \langle ES\hat{k}^- | D^{(n)} | X \rangle d^2\hat{k}.
\]

In these equations, \(|X\rangle\) is the ground state and \(|ES\hat{k}^-\rangle\) is the excited state for channel \( S \), energy \( E \) and momentum unit vector \( \hat{k} \). The integrals are over the scattering angles of the products, \( \theta \) and \( \phi \). Writing \( \langle g^2 \rangle = \lambda^2 \langle f^2 \rangle \), where \( \lambda \) is a real number, we obtain

\[
M = \frac{2}{\lambda + \lambda^{-1}} \frac{\langle fg \rangle}{\sqrt{\langle f^2 \rangle \langle g^2 \rangle}}.
\]

The Schwarz inequality assures that \( 0 \leq M \leq 1 \). Equation (7) also shows that \( |\lambda| > 0 \) is a necessary condition for modulation. In other words, the signal produced with both laser beams present must be greater than that obtained with either laser alone, which was the case for all the molecules studied here. (Averaging the signal over the axial coordinate of the laser in the region where the laser and molecular beams overlap reduces \( M \) by approximately a factor of two [4].) This effect limits the ability to measure very weak modulations but otherwise is not essential for the present discussion.) Next, we expand \( f \) and \( g \) in a spherical basis,

\[
f = \sum_{j,m} A_{j,m} Y_{jm}(\theta, \phi)
\]

and

\[
g = \sum_{j,m} B_{j,m} Y_{jm}(\theta, \phi),
\]

where \( Y_{jm} \) are spherical harmonics. (The angular momentum indices \( j \) and \( m \) should not be confused with \( m \) and \( n \) in the dipole operators.) Assuming \( f \) and \( g \) are both normalized, we obtain

\[
M = \frac{\lambda}{1 + \lambda^2} \sum_{j,m} (A_{j,m}^* B_{j,m} + A_{j,m}^* B_{j,m}).
\]
The magnitude of $M$ depends on the distribution over $m$. For a uniform distribution over $m$ with $\lambda = 1$, 100% modulation is obtained. On the other hand, if, for example, the nonzero $A_{j,m}$ coefficients are clustered around $|m| = j$, and the nonzero $B_{j,m}$ coefficients are clustered around $m = 0$, there will be little modulation. The distributions over $m$ are determined by the symmetry properties of the intermediate states in the multiphoton dipole transitions, which borrow their intensities from available rotational, vibrational and electronic states \cite{30}. Differential cross-section measurements with just one of the laser fields present could provide these distributions. We expect these distributions to depend on the energies of the intermediate states. We note that Wang \textit{et al} \cite{31} observed modulation of the parent ion of trimethyl amine produced by interference between $5\omega_1$ and $2\omega_1 + \omega_3$ pathways at fundamental wavelengths between 601.5 and 602.8 nm, whereas no modulation was detected here at 532 nm ($4\omega_1$ versus $\omega_3 + \omega_1$).

5. Conclusions

Coherent phase control of the photoionization and photodissociation of acetone, DMS, and 1,1-dichloroethylene was obtained, using 532 and 177 nm radiation to initiate two-pathway interference. Strong phase modulation of the products demonstrated that the high densities of states and multiple reaction channels do not reduce the controllability of these complex molecules. The phase lag between different pairs of products from DMS and acetone was measured as a function of the location of the laser focus. Information obtained from the channel phases of the photoproducts and the spatial phase of the laser was used to elucidate the reaction mechanisms. The absence of modulation for other molecules may be a consequence of the symmetry of intermediate states.

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