**Convenient (1+1) probe of S(¹D₂) and
application to photodissociation of carbonyl sulfide at 216.9 nm**

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Abstract

We introduce a 1+1 probe of S(¹D) at 216.9 nm through the (4s ³S^o) state, and demonstrate it in one-color experiments to examine the photodissociation of OCS using DC slice imaging. As seen in previous work, the S(¹D) image shows a bimodal distribution corresponding to two dissociation pathways of the parent molecule. The slice images are rotationally resolved across the entire product velocity profile. Separate two-color experiments allow us to determine that the probe is insensitive to orbital polarization in the sulfur atom under the conditions studied.

Introduction:

Carbonyl sulfide is the most abundant sulfur-containing molecule in the atmosphere and a precursor of sulfate aerosols[1]. It also acts as an important species in stratospheric ozone depletion[2]. It has been detected in dense interstellar clouds and in comets[3, 4] and identified as a possible mediator of prebiotic peptide formation[5]. Studies on OCS photodissociation has been carried out extensively using Laser Induced Fluorescence (LIF)[6, 7] and ion imaging techniques[8-13] to investigate nature of their products, explore the reaction dynamics, and elucidate environmental impacts. $S(^1D_2)$ is the dominant product of OCS photodissociation in the ultraviolet, and it is usually probed by 2+1 resonance enhanced multiphoton ionization (REMPI) through the $4(^1P)$ state or the $4(^1F)$ state at 291.5nm or 288.2 nm, respectively[10, 14]. In this letter we describe a convenient 1+1 probe of $S(^1D_2)$ through the $4s(^3S^o)$ level and apply it to photodissociation of OCS at 217 nm. We also take the opportunity to introduce modifications of our Rydberg time-of-flight instrument to allow for high-resolution slice imaging.

OCS is a linear triatomic, 16 valence electron system, isoelectronic with molecules such as CO_2 , N_2O and CS_2 . The first absorption band of OCS extends from 200 nm – 250 nm [6, 15, 16]. Upon absorption of a photon, OCS ($X^1\Sigma^+$) dissociates to give vibrationally cold and rotationally hot CO ($X^1\Sigma^+$) along with S (1D_2) or S (3P_J) at a branching ratio of 95:5, through A' ($^1\Delta$) and A'' ($^1\Delta$ and $^1\Sigma^-$) excited states. The dipole transition from the ground state ($^1\Sigma^+$) to excited states ($^1\Sigma^-$ and $^1\Delta$) are forbidden in the linear geometry, but weakly allowed in bent geometry[17]. As a result, the molecule shows greatly enhanced absorption at the red end of the spectrum with increasing temperature[18]. The three excited states involved in the absorption are: an A'' state arising from C_s deformation of the $^1\Sigma^-$ state (hereafter

referred to as the “B” state) and two Renner-Teller components, A' (“A”) and A'' (“C”) arising from deformation of the $^1\Delta$ state. The transition dipole moment is parallel to the molecular plane when dissociating from the A' state and perpendicular for A'' states.

Extensive theoretical studies for the OCS photodissociation were performed by many groups [9, 19-22]. Suzuki and coworker[9] reported a comprehensive theoretical and experimental study of the ultraviolet photodissociation of OCS with ion imaging of both the ground state sulfur atom and the dominant singlet channel, just prior to the advent of velocity map imaging. The image for S (1D_2) showed two speed components confirming a bimodal rotational distribution of CO ($X^1\Sigma^+$) fragment reported earlier by Sato and coworkers[8]. The faster, low-J component was ascribed to an admixture of dissociation from the A and B states, yielding a nearly isotropic angular distribution. They found that on changing UV wavelengths from 223nm to 248nm, the angular distribution of the faster component became more perpendicular, suggesting that the contribution from the A state decreases with decreasing excitation energy. This was reinforced by results from Kim et al.[11], who showed that hot-band excitations at the long wavelength tail of the first absorption band gave nearly pure perpendicular angular distributions. Throughout this wavelength region the inner, slower component showed a nearly pure parallel angular distribution. Schinke and coworkers[23] analyzed the first absorption band of OCS at 222nm and calculated the PES for the four lowest singlet state and four lowest triplet states, along with the transition dipole moments and absorption cross sections[24]. They concluded that both the A state and the B state contribute to the absorption at the peak, with the B state contribution roughly half that of the A state. At the long wavelength tail, the A state component dies away and only the pure perpendicular B

state remains. Schinke and coworkers also reported wavepacket calculations with trajectory surface hopping treatment of the nonadiabatic transition from the A state to the ground state. These confirmed the earlier suggestion from Suzuki and coworkers that the slow, parallel component associated with lower rotational levels arose from nonadiabatic transitions of a subset of the A state population that accesses a crossing seam at intermediate OC-S distances.

Experimental Section:

Although a detailed description of the experimental setup has been reported in our previous papers focused on Rydberg time-of-flight of spin-polarized hydrogen atoms [25, 26], extensive modification of the ion optics for DC slice imaging have been implemented and will be described here. The apparatus consists of two differentially pumped chambers. The main chamber is a “spherical octagon” (Kimball-Physics) connected on both sides to “tees” on which are mounted the beam source and the detector. Both chambers are pumped by magnetic-bearing turbomolecular pumps. The molecular beam of 2% OCS in argon is introduced through a piezoelectric disk valve[27] mounted in the source chamber and skimmed once before entering the main chamber. The valve was operated at 10Hz with nominal pulse width of 120 μ s and 1050 torr backing pressure. With the beam on, the pressure was $\sim 1 \times 10^{-5}$ torr and 9×10^{-7} torr in source chamber and reaction chamber, respectively.

The ion optics setup for DC slice imaging [28-31] is mounted on the main chamber using the grooves provided. The ion lens system consists of four elements, namely repeller, lens 1 (extractor), and two additional lenses, all fabricated from 4 inch outer diameter and 0.1 inch thick stainless steel plates. Inner diameters and plate separations for optimum velocity focusing were calculated using SIMION 7.0

software[32] and the dimensions are given in Fig. 1. The interaction region is in the middle between the repeller and the extractor lens, where the supersonically expanded molecular beam is crossed by counter propagating laser beams at right angles. Optimum voltage ratios needed for sharp velocity focusing and a large degree of expansion of the ion cloud along the TOF axis were $V_{L1} \approx 0.86V_R$ and $V_{L2} \approx 0.54V_R$, while $V_R=1\text{kV}$ and L_3 is grounded. This arrangement is capable of giving very high resolution in DC slice imaging experiments as will be seen below.

Fig. 1. Ion optics setup

At the very end of the reaction chamber resides the position sensitive detector, which consists of a matched pair of 75mm diameter microchannel plates (MCPs) coupled to a P-47 phosphor screen. The front plate was kept at ground potential, while the back plate was pulsed from $\sim 1400\text{V}$ to $\sim 2400\text{V}$ by means of a high voltage pulse generator. Positive voltages were given to both bias (-HV) and pulse (+HV) of the pulse generator, therefore, a pickup box containing $5\text{k}\Omega$ resistor was connected to drain the excess current. The phosphor screen was held at $+5\text{kV}$. All delays were controlled by a delay generator that

could manipulate the gate pulse delay and width to selectively detect fragments of specific masses based on their time of arrival at the detector. Narrow time gates increase the image resolution by slicing a narrower segment of the expanding ion cloud but ultimately the slice width it is limited by the pulse duration of laser (~8ns). With the current setup, a time gate of 55ns was used for slicing the S^+ product. Finally, the image was captured using a CCD camera and recorded in the computer using our own NuAcq centroiding software. A photomultiplier tube was incorporated viewing the detector to monitor timing information.

For one-color experiments, both photodissociation and probe was achieved using 216.9 nm light generated by frequency mixing the third harmonic of the Nd^{3+} :YAG laser (355nm) with 555nm light produced from a tunable dye laser (Pyrromethene 580). The dye laser was pumped by the 532 nm second harmonic of the same YAG laser. The maximum output power for 216.9nm light was ~2.0 mJ/pulse at 10 Hz repetition rate. Initial horizontally polarized light was rotated by a periscope and the resulting vertically polarized light (parallel to detector face) was focused to the interaction region of the reaction chamber through a fused silica lens ($f = 230\text{mm}$). The probe laser wavelength was monitored using a wavemeter.

In two-color experiments, photodissociation was performed using 222 nm light. This light was generated by frequency mixing of 355nm (third harmonic of the seeded Nd:YAG laser) with the 593 nm output of a dye laser (Sulforhodamine B) pumped by the same Nd:YAG, giving ~1.0 mJ/pulse. The vertically polarized 222nm light was focused to the interaction region by a fused silica lens ($f = 130\text{mm}$).

For polarization sensitivity measurements, ~0.2 mJ/pulse pure vertical and horizontal light was produced using a set of optics. First, the probe light passed through an alpha-BBO Glan Polarizer that

produced near-pure vertical polarization. Next the vertically polarized beam was sent through a Berek's Polarization Compensator (Model 5540) set at half-wave retardation and the resultant light was monitored using a MgF₂ Rochon prism to obtain either pure horizontal or vertical polarization by changing the orientation scale of the compensator.

Results and Discussion:

OCS probing at 216.9 nm: OCS was dissociated and probed at the same wavelength, 216.9 nm, where it has an absorption cross-section of 2.5×10^{-19} cm² molecule⁻¹ [33]. DC slice imaging of the S(¹D₂) photoproduct was effected by resonance enhanced multiphoton ionization (REMPI) through the following 1+1 excitation scheme at 46092.20 cm⁻¹ (216.89 nm, air):

This is a spin-forbidden transition which is facilitated by the spin-orbit interaction in sulfur. In spite of being nominally forbidden, we find it a fairly sensitive probe scheme. During the acquisition, the probe laser frequency was scanned over the entire Doppler width of the sulfur atom product caused by the recoil velocity. The resulting raw sliced imaging is shown in Fig. 2a. It is largely consistent with the previous studies in this wavelength region [8-10, 12].

Fig. 2. a) S(¹D) from one-color photodissociation and probe of OCS at 216.9nm. b) Corresponding total translational energy distribution. The comb above reflects the co-fragment CO(v=0) rotational distribution.

As described originally by Sato et. al.,[8] the co-fragment CO ($v=0$) has a bimodal distribution. In their REMPI spectra for the photodissociation of OCS at 217nm there are two distinct regions, faster fragments corresponding to low J values (peak $J \sim 56$) and slow CO that has high J values (peak $J \sim 65$)[8, 10]. This bimodal nature is exhibited in our image (Fig. 2a), but we find in the translational energy distribution that slower fragments peak at $J=71$ and faster fragments at $J=59$.

The S(¹D₂) angular distribution following dissociation in the wavelength region is strongly anisotropic[12]. The photofragment angular distribution for one-photon absorption may be characterized by the equation $I(\theta) = (4\pi)^{-1}[1 + \beta P_2(\cos \theta)]$ [34, 35], where θ is the angle between polarization axis of the light and velocity of one fragment and P_2 is the second Legendre polynomial. The anisotropy parameter β thus defines the angular distribution[36]. In the axial recoil limit it may be related to the angle χ between the fragment recoil direction and transition dipole moment (in the molecular frame): $\beta = 2P_2(\cos \chi)$. β has

limiting values of -1 and 2 for pure perpendicular and parallel transitions respectively. The overall angular distribution for this dissociation is $\beta = 1.5$, which means overall the transition is mostly parallel. Photofragment angular distributions were calculated separately for the two velocity regions, yielding anisotropy parameters of 1.20 and 2 for the faster and slower components, respectively, largely consistent with previous results. The $S(^1D_2)$ recoil speed distribution is plotted with the speed-dependent anisotropy parameter in Fig. 3.

Fig. 3. Speed and anisotropy parameter distributions for 216.9 nm dissociation of OCS.

Photodissociation of OCS in this region is known to produce $S(^1D)$ that possesses significant orbital polarization. An important question concerning this probe transition is its sensitivity to this polarization. To assay this, we used a two-color configuration so that we could independently manipulate the polarization of the probe without affecting the photolysis light. Fig. 4 shows the two-color image of $S(^1D)$ using 222nm for photodissociation and (1+1') REMPI probing. The polarization study was performed using two linearly polarized lasers, 222nm and 216.9 nm counter-propagating to each other.

OCS was dissociated using 222nm light and resultant S(¹D) fragments were probed using (1+1') REMPI scheme as follows:

Figure 4 shows images with vertical photolysis polarization and either vertical or horizontal probe polarization. The difference of these two images is also shown.

Fig. 4. S(¹D₂) images for two laser experiments with photodissociation at 222nm and probe laser at 216.9 nm with two polarization geometries a) horizontal probe laser polarization. b) Vertical probe laser polarization. c) Difference of images a) and b).

There is no apparent change in the images upon changing the probe polarization. At this photolysis wavelength, Suzuki and coworkers reported profound changes in the image appearance upon changing the probe polarization when using the (2+1) probe at 292nm[12]. The S(¹D₂) orbital polarization from OCS dissociation was also characterized by Rakitzis et al. in this region[10], by Brouard at 248 nm[37], and by Lee et al. at 193nm[13]. Our images do not show any significant change for two polarization geometries, indicating that under these conditions, this probe transition is not sensitive to the polarization of the S(¹D) photofragment.

As the probe is not sensitive to polarization, we could use it to measure the angular distribution at 223 nm free of alignment effects. We find that here the higher energy component of this image is more isotropic, with $\beta = 0.59$ compared to the result at 217 nm, which has a β of 1.20. Suzuki had reported a value of 0.7 for the fast component, after accounting for alignment effects, in reasonable agreement with our result. This declining anisotropy in the fast component with increasing photolysis wavelength is consistent with the declining relative contribution of the A state with decreasing excitation energy.

Figure 5. Power dependence of linewidth determined from Doppler width of unscanned image.

We also performed a one-color experiment to examine the effect of laser power on linewidth for the transition. In this case we fixed the laser frequency on the center of the transition and monitored the effective width as a function of laser power. To determine the linewidth, we recorded an image

and projected the signal along the laser propagation axis. We divided this signal by a similar projection of the full scanned image to account for the variation in signal intensity across the image. We then converted this to velocity along the laser propagation direction using the normal image velocity calibration. Finally, by invoking the Doppler expression, we could convert this to frequency. These spectra were then fitted to Gaussians to determine the linewidth. The results are shown in Fig. 5. Modest power broadening was observed even at probe powers as low as 0.07 mJ/pulse.

In summary, we have introduced a convenient 1+1 probe of $S(^1D_2)$ and applied it to the photodissociation of OCS at 217nm. We showed that this probe, in conjunction with the new DC slicing ion optics introduced to the apparatus, allow for a rotationally resolved translational energy distribution across the full product velocity profile. The results we obtain show a more anisotropic angular distribution for the fast component, consistent with a greater B state contribution to absorption at 217 nm compared to longer wavelengths as expected. We saw no sensitivity to $S(^1D_2)$ orbital alignment under the conditions of the study. Finally, we examined the power dependence of the linewidth and observed modest power broadening even at the lowest power employed.

Acknowledgments

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