Combining VUV lasers with the Time-Sliced Velocity-Mapped Ion Imaging Method for studying the photodissociation of small molecules

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Abstract

We report on an experimental method for the study of extreme ultraviolet (EUV) and vacuum ultraviolet (VUV) photodissociation dynamics of small molecules using time-sliced velocity-mapped ion imaging (TSVMI) detection. The four-wave resonant sum and difference-frequency mixing (FWRSDFM) method is used to provide a relatively intense high repetition rate light source in this region. These two methods are used to study the photodissociation of N_2, NO, and CO_2 in the energy ranges of 13.0-13.7 and 9.6-10.3 eV. The results indicate that this is a viable method for the study of these molecules in this wavelength region.

1. Introduction

The EUV and VUV regions are the spectral regions where there are strong absorption bands of small molecules and their atomic fragments that are important in planetary atmospheres, the interstellar region and in the circumstellar envelope [1]. Thus, to dissociate the molecules and detect the fragments that are formed one needs intense light sources that can be combined with a sensitive detection method. The FWRSDFM method provides a relatively intense high repetition rate light source in this region. If this is coupled with the highly sensitive TSVMI method then one can measure the identity of the products, their recoil velocities and their angular distributions. This information is then used to sort out the processes that are occurring when a molecular beam containing supersonically cooled simple molecules are irradiated with the unfocused light produced by the FWRSDFM.

2. Experimental

The TSVMI apparatus has been previously described in detail [2]. Hence, only a brief description will be presented here. A pulsed supersonic beam of N_2, NO,

supersonically cooled sample of the gas to the interaction region of the TSVMI apparatus where light produced by the FWRSDFM is also present. This light is generated by focusing lasers with the frequencies ω_1 and ω_2 into a Kr jet to form EUV and VUV light at the frequencies $2\omega_1+\omega_2$ and $2\omega_1-\omega_2$ by the FWRSDFM method. The light expanding from the jet passes through apertures into the interaction of the TSVMI apparatus and since there is no wavelength separation device between the jet and the interaction region there is also light at the frequencies ω_1, $3\omega_1$ and ω_2. The ω_1 is tuned to one-half of the two-photon resonance of the Kr $(^5P_{1/2})$ level at 94,092.86 cm^{-1}, while ω_2 is from a tuneable visible laser 654.15 to 645.70 nm (15,287 to 15,487 cm^{-1}). This light covers the energy ranges of 13.0-13.7 and 9.6-10.3 eV in the EUV and VUV regions, respectively. The ion signal described in this work can only be observed in the TOF mass spectrum by injecting the four-wave mixing gas, indicating the dissociation and ionization processes come from the contributions of $2\omega_1+\omega_2$, $2\omega_1-\omega_2$ or $3\omega_1$.

3. Results

Single photon photodissociation of N_2 from the $o^1\Pi_u$, v' = 2 and b' $^1\Sigma_u$, v'=8 excited states were done for the first time using light generated by the FWRSDFM. Figure 1 shows the velocity-mapped sliced image of the R(0) (J'=1) rotational line (109,565.1 cm^{-1}) of $o^1\Pi_u$ ($v = 2$) band, obtained by using a 40 ns gate time to capture the central part of the broadened N^+. The total $P(E_T)$ plot is obtained from the image, as shown in Figure 1. Only one sharp peak is observed at a kinetic energy of 1.43 eV. This peak is at an energy that corresponds to the formation of the atomic products $N(^2D°) + N(^4S°)$ that can only be formed after intersystem crossing from the singlet state to a triplet state. The images, β parameters and total kinetic energy release plots have been obtained for 37 rotational transitions in the P, Q, and R branches of the $o^1\Pi_u$, v' = 2 and b' $^1\Sigma_u$, v'=8 excited states of N_2 and they are used to show that the EUV photon both dissociates N_2 and ionizes $N(^2D)$.

The single photon dissociation of CO_2 was studied by tuning ω_2 so that the $2\omega_1+\omega_2$ energy equalled 13.4463 eV that corresponds to autoionization line of O ($^1D_2^o$) corresponding to $2s^22p^3(^2D_{3/2})3d,^1D_2 \leftarrow$ O ($^1D_2^o$) transition. The slice image and the plot of total kinetic release (TKER) derived from this slice image is shown in Fig. 2. This is a more complex plot than the one shown for the N(^{2}D) from N_2 but the observed structure is clearly reproducible. It probably represents the internal energy distribution of the CO molecule that is also produced in the photodissociation at this energy.

The O ($^1D_2^o$) atom was also detected from the photodissociation of NO at 13.4463 eV. The strong peak in the NO in the TKER plot that is obtained from the image in Fig. 3 is at 2.5 eV with a very anisotropic angular distribution. This peak has been identified as due to the dissociation channel, NO (X $^2\Pi_{3/2}$) + $h\nu_{sum}$ (13.4463 eV) $\rightarrow$ N ($^2D^o$) + O ($^1D_2^o$). The peaks at lower energies are probably due to dissociation of the NO dimer that is known to be present in gas phase NO. At other wavelengths we have been able to detect the N(^{2}D) atom formed from the photodissociation of NO that allows to gain a different perspective of the dynamics in this energy range.
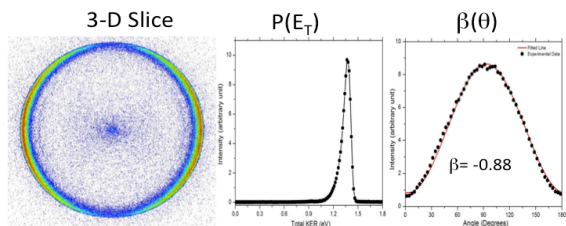
3. Figures

Figure 1: 3-D slice image, P(E_T) and the angular distribution for the predissociation of N_2 via the following reaction, N_2 (X $^1\Sigma_g$, v" = 0, J" = 0) + $h\nu_{VUV}$ $\rightarrow$ N_2 (o$^1\Pi_u$, v' = 2, J' = 1) $\rightarrow$ N(^{2}D) + N(^{4}S).
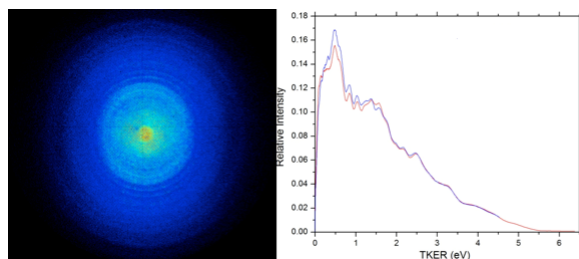

Figure 2. 3-D sliced image of O^+ and its P(E_T) obtained from CO_2 by setting the EUV energy to the autoionization line of O ($^1D_2^o$): $2s^22p^3(^2D_{3/2})3d$ $^1D_2$ $\leftarrow$ O ($^1D_2^o$) which is at the energy of 13.4463eV. The Blue and red curve show the TKER curve for two different runs.
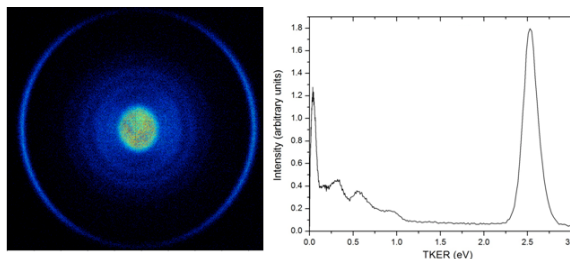
Figure 3. 3-D sliced image of O^+ and its P(E_T) obtained from NO by setting the EUV energy to the autoionization line of O ($^1D_2^o$): $2s^22p^3(^2D_{3/2})3d$ $^1D_2$ $\leftarrow$ O ($^1D_2^o$) which is at the energy of 13.4463eV. The strong peak at 2.5 eV has been identified as the dissociation channel, NO (X $^2\Pi_{3/2}$) + $h\nu_{sum}$ (13.4463 eV) $\rightarrow$ N ($^2D^o$) + O ($^1D_2^o$).

6. Summary and Conclusions

We have shown that combining four-wave resonant sum and difference-frequency mixing (FWRSDFM) to provide a pulsed light source in the EUV and VUV region with time-sliced velocity-mapped ion imaging (TSVMI) detection provides an excellent way to study photodissociation dynamics in this spectral region. From the results that have been obtained thus far it is clear that having more flexible in the ionization of the product atoms would expand the current capabilities in our laboratory. We are currently adding this to the present setup so that we will be able to independently vary the photolysis and the detection wavelengths.

Acknowledgements

References

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