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2008

document version

Publisher's PDF, also known as Version of record

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citation for published version (APA)

Lipciuc, ML. (2008). *High resolution slice imaging of nonadiabatic state-to-state photodynamics*. [PhD-Thesis - Research and graduation internal, Vrije Universiteit Amsterdam].

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Summary

High resolution slice imaging of nonadiabatic state-to-state photodynamics

Absorption of photons by molecules opens various molecular decay channels. The breaking of a molecular bond due to the exposure to light is a common definition of the photodissociation process. The difference between the photon energy and the bond dissociation energy, known as the excess energy, may be distributed among all available degrees of freedom of the nascent fragments (translational and internal). The proportion of the excess energy released as kinetic energy as well as the masses of the nascent photofragments will determine their recoil speed. The residual excess energy is distributed over the other degrees of freedom of the fragments and may lead to rotational, vibrational and electronic excitation of the fragments. Velocity map slice imaging technique is a powerful tool for studying the gas phase molecular reaction dynamics. This technique allows simultaneous measurement of the rotational, vibrational, electronic and translational energy distribution of the products of a unimolecular reaction and it is used in this thesis to investigate the reaction of gas phase molecule with light.

The design of an electrostatic ion lens for photodissociation of spatially oriented parent molecules in combination of slice imaging of the angular distribution of photofragments is presented in Chapter 2. With the slice imaging technique the spatial distribution of oriented recoiling photofragments can be measured without symmetry restriction and with high resolution. The orientation electrodes are inserted in between the repeller and the extractor electrodes of the ion lens. The dimensions and position of the orientation electrodes are very important since its presence will distort the electric field within the ion lens and will affect the ions trajectories. The combination of molecular orientation and velocity map slice imaging is experimentally demonstrated on the dissociation of rotationally state-selected and spatially oriented CD_3I at 266 nm and the (2+1) REMPI detection of the CD_3 photofragments. This orientation ion lens provides slice imaging of photofragments from oriented photodissociation with good quantitative accuracy. In Chapter 3 the experimental design and performance of the large frame centroiding imaging detector for high-resolution velocity map slice imaging of photofragments is described in detail. The detector combines fast gain gating and on-the-fly centroiding of ion events. The intensity distribution of individual light spots is con-

verted to position information with sub-pixel accuracy. The limit for the spatial resolution becomes the MCP pore diameter. We use the centroiding imaging detector to measure the three-dimensional speed distribution of CD_3 fragments after the photolysis of CD_3I and its performance is described in In Chapter 4. For the detection of the CD_3 photofragments we used a two-color REMPI scheme to reduce the broadening of the speed distribution due to the electron kick on the ionic CD_3^+ in the ionization step. The final Full-Width-Half-Maximum speed resolution that we obtain is $1.9 \cdot 10^{-3}$, at present the best resolution ever reported in ion imaging experiments.

In Chapter 5 we report slice imaging experiments for the quantum state-to-state photodissociation of ground state and vibrationally excited OCS molecules near 230 nm. From one color experiments detecting single $\text{CO}(J)$ fragments we observe photodissociation of vibrationally excited OCS molecules with up to two quanta excited in the bending vibration. A dissociation channel in which the $\text{CO}(J)$ fragments are correlated with ground state S^3P atoms is observed in the high rotational excitation region of the CO fragments. Two-color experiments detecting single $\text{CO}(J)$ fragments show a strong decrease in the β parameter from a large positive to a large negative value with a small reduction of about 1000 cm^{-1} in the photodissociation energy. The strong change in β parameter is attributed to a breakdown of the axial recoil, which causes a large increase in the molecular frame deflection angle at very low recoil velocity. For the CO fragments detected in the $J=64$ rotational state, the molecular frame deflection angle increases from 40° to 95° when the anisotropy parameter decreases from $\beta=1.91$ to -0.52 . Two-color experiments detecting the S^1D_2 fragments reveal, at high resolution, the internal state distribution of the $\text{CO}(J)$ co-fragments, and the effect of the polarization of the probe laser on the resolution of the slice images. With the polarization of the probe laser we can direct the electron kick that the ion gets during ionization process. Changing the polarization of the probe laser from parallel to perpendicular to the slice imaging plane will reduce the broadening of the velocity resolution by the electron recoil kick. The dissociation energy of OCS molecule is determined with a relative accuracy of about $7 \cdot 10^{-4}$.

The state-to-state cross section for the photodissociation of rovibrational bending states of OCS is presented in Chapter 6. Using hexapole quantum state-selection of $\text{OCS}(v_2=0,1,2|JM)$ and high-resolution slice imaging of quantum state-selected $\text{CO}(J)$ the state-to-state cross section $\text{OCS}(v_2=0,1,2|JM) + h\nu \rightarrow \text{CO}(J) + \text{S}^1\text{D}_2$ was measured for bending states up to $v_2=2$. The population density of the state-selected $\text{OCS}(v_2=0,1,2|JM)$ in the molecular beam was obtained by (2+1) REMPI via the $(^2\Pi_{3/2})4p\pi^3\Delta \leftarrow \leftarrow \tilde{X}^1\Sigma^+ 0_0^0, 2_1^1$ and 2_2^2 vibronic transitions and comparison with room temperature bulk gas. The cross section is found to vary with the final CO rotational state. A strong increase of the cross section with increasing bending state is observed for $\text{CO}(J)$ in the high J region, $J=60-67$. Integrated over all J states we find $\sigma(v_2=0) : \sigma(v_2=1) : \sigma(v_2=2) = 1.0 : 7.0 : 15.0$. A quantitative comparison is made with the dependence of the transition dipole moment function on the bending angle.

In Chapter 7 we report the polarization of S^1D_2 angular momentum after the photolysis of rovibrational state-selected $\text{OCS}(v_2=1|JIM=111)$ molecule at 234.68 nm. The high resolution of the slice imaging experiment makes it possible to extract alignment moments

of $S(^1D_2)$ fragments correlating with single rotational channels in $CO(J)$. The $S(^1D_2)$ fragments are detected by (2+1) REMPI ionization *via* the 1P_1 and 1F_3 resonant intermediate states. Data were recorded in five pump-probe laser geometries which were sufficient in order to obtain the alignment moments of the $S(^1D_2)$ photofragment. The angular distribution of the $S(^1D_2)$ velocity rings are extracted and analyzed using two different polarization models. In the high J region it appears that a dynamical model on a single potential energy surface, including non-axial recoil dynamics, is best suited to fit the experimental polarization data. From the molecular frame alignment moments the m -state distribution of $S(^1D_2)$ is calculated as a function of $CO(J)$ channel. A comparison is made with the theoretical m -state distribution calculated from the long-range electrostatic dipole - dipole plus quadrupole interaction model. The $S(^1D_2)$ photofragment velocity distribution shows a very pronounced single peak for fragments born in coincidence with $CO(J=61)$.

Photodissociation experiments on rotationally state-selected CH_3Br and CD_3Br at 213 nm and near 230 nm are reported in Chapter 8. The velocity distribution of the methyl fragment shows a rich structure, especially for the CD_3 photofragment, assigned to the formation of vibrationally excited methyl fragments in the ν_1 and ν_4 vibrational modes. The CH_3 fragment formed with ground state $Br(^2P_{3/2})$ is observed to be rotationally more excited, by some $230\text{-}340\text{ cm}^{-1}$, compared to the methyl fragment formed with spin-orbit excited $Br(^2P_{1/2})$. Branching ratios and angular distributions are obtained for various methyl product states and they are observed to vary with photodissociation energy. The nonadiabatic transition probability is calculated from the images and differences between the isotopes are observed. An enhanced nonadiabatic transition probability is found for the state-selected $K=1$ methyl bromide parent molecule versus non state selected parent molecule. The bond dissociation energy for both isotopes was determined from the state-to-state photodissociation experiments.