

MO 17: Stossprozesse, Energietransfer 2

Zeit: Mittwoch 16:30–17:45

Raum: VMP 6 HS-G

MO 17.1 Mi 16:30 VMP 6 HS-G

A new CD3 REMPI transition accidentally found by imaging spectroscopy — ●JENS RIEDEL¹ and KOPIN LIU² — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Institute of Atomic and Molecular Sciences (IAMS), Academia Sinica, Taipei, Taiwan

In the course of a crossed beam imaging study of the reaction dynamics of $\text{Cl} + \text{CHD}_3(1_13_1) \rightarrow \text{HCl} + \text{CD}_3$, an unexpected ring-like feature was observed on the CD_3 ground state (0_0) product image. Using the technique of ion imaging spectroscopy, the mysterious feature was tentatively ascribed to the formation of the vibrationally excited $\text{CD}_3(3_14_1)$ product from the above combination-band excited reaction. The intriguing aspect of the present finding is that the corresponding (2+1)-REMPI band of $\text{CD}_3(3_14_1)$ appears totally hidden by the more intense $\text{CD}_3(0_0)$ origin band, yet the two-dimensional nature of ion imaging technique enables us to decipher its spectral character and extract the otherwise lost dynamical information.

MO 17.2 Mi 16:45 VMP 6 HS-G

Host-guest porphyrin-phthalocyanine self-assembled supramolecules as artificial photosynthetic system — ●ROEL MENTING¹, EUGENY ERMILOV^{1,3}, JANET LAU², DENNIS NG², and BEATE RÖDER¹ — ¹Institut für Physik, Photobiophysik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin — ²Department of Chemistry and Centre of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China — ³Institut für Physiologie, Campus Benjamin Franklin, Charité * Universitätsmedizin Berlin, Arnimallee 22, D-14195 Berlin

Complexes of porphyrins and phthalocyanines are well suited for modeling both the electron and energy transfer processes in photosynthetic reaction centers.

We used supramolecular approach to build hetero-arrays of beta-cyclodextrin-conjugated silicon phthalocyanine (CD-Pc) with CD-conjugated silicon subphthalocyanine (CD-subPc) and tetrasulfate porphine (TPPS) by host-guest interactions. The absorption of resulting 1:1:1 supramolecular complex covers a broad region of the solar spectrum starting from 350 nm and up to 700 nm. By means of steady-state and time-resolved optical spectroscopy it was found that the photophysical properties of these supramolecules are strongly affected by two different types of interactions between their parts, namely photoinduced charge transfer (CT) and excitation energy transfer (EET). The efficacy of these processes in population/depopulation dynamics of TPPS, CD-Pc and CD-subPc excited states after light absorption is discussed.

MO 17.3 Mi 17:00 VMP 6 HS-G

Quantum dynamics of the nucleophilic substitution in methyl iodine — ●MARKUS KOWALEWSKI and REGINA DE VIVIE-RIEDLE — Department Chemie und Biochemie, Ludwigs-Maximilians Universität München

We investigate the gas phase dynamics of the anion-molecule nucleophilic substitution reaction of chloride and methyl iodine [1]. Our theoretical methods based on quantum chemical ab initio calculations involve selected degrees of freedom which are treated with wave function methods in the Schrödinger picture.

The low energy reactions dynamics show the formation of a weakly bound anion-dipole complex. Moreover the calculations clarify the role of spectator modes which have a significant contribution to the effective barrier in the gas phase substitution reaction. With a different set

of coordinates we gain insight into more unusual reaction pathways.

[1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, R. Wester, *Science* **319**, 183 (2008).

MO 17.4 Mi 17:15 VMP 6 HS-G

An analytic model of molecular collisions in fields — ●MIKHAIL LEMESHKO and BRETISLAV FRIEDRICH — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

We present an analytic model of thermal state-to-state rotationally inelastic collisions of molecules in electric, magnetic and radiative fields. The model is based on the Fraunhofer scattering of matter waves and requires Legendre moments characterizing the “shape” of the target in the body-fixed frame as its input. External fields orient or align the target in the space-fixed frame and thereby effect a striking alteration of the dynamical observables: both the phase and amplitude of the oscillations in the partial differential cross sections undergo characteristic field-dependent changes that transgress into the partial integral cross sections. As the cross sections can be evaluated for a field applied parallel or perpendicular to the relative velocity, the model also offers predictions about steric asymmetry. The model has been developed for collisions of (i) closed shell atoms with polar $^1\Sigma$ and $^2\Pi$ molecules in electrostatic fields; (ii) closed-shell ions with polarizable $^1\Sigma$ molecules in laser fields; (iii) closed-shell atoms with paramagnetic $^2\Sigma$, $^3\Sigma$ and $^2\Pi$ molecules in magnetic fields. We exemplify the field-dependent quantum collision dynamics with the behavior of the Ar-NO($^2\Pi$) system in an electrostatic field and He-CaH($^2\Sigma$) system in a magnetic field. A comparison with close-coupling calculations available for the former system [Chem. Phys. Lett. **313**, 491 (1999)] demonstrates the model’s ability to qualitatively explain the field dependence of all the scattering features observed.

MO 17.5 Mi 17:30 VMP 6 HS-G

QCT calculation for Sr+CH₃Br/CH₃I→SrBr/SrI+CH₃ — ●VICTOR WEI-KEH WU^{2,3}, XIAO-XUE ZHAO¹, and YA-MIN LI¹ — ¹School of Environmental and Chemical Engineering, Dalian 116028, People’s Republic of China — ²Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — ³Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, 33602 Bielefeld, Germany

The first QCT calculation for both exothermic reactions $\text{Sr} + \text{CH}_3\text{Br}/\text{CH}_3\text{I}$ (0.4 eV) is carried out based on constructed LEPS potential energy surfaces (PES). Integral and differential (including vibrational energy, scattering angle distribution and rotational alignment) reactive cross sections dependent upon energy after Teule’s experiment in 1996 have been obtained, where reaction $\text{Sr} + \text{CH}_3\text{Br}$ shows attractive from $r_{\text{Sr-Br}}=9 \text{ \AA}$ and then with a slight well; reaction $\text{Sr} + \text{CH}_3\text{I}$ shows typically attractive from $r_{\text{Sr-I}}=5.5 \text{ \AA}$. The reactive cross sections can be well simulated with the combination of weights of AD-LOC of Bernstein and Eu of Eu models. The respective Sato parameters are: $S_{\text{Sr-Br}}=0.145$, $S_{\text{Br-CH}_3}=0.3$, $S_{\text{Sr-CH}_3}=-0.09$; $S_{\text{Sr-I}}=0.30$, $S_{\text{I-CH}_3}=-0.06$, $S_{\text{Sr-CH}_3}=-0.41$. Both SrBr and SrI are scattered backwards, where SrI is more strongly than SrBr. The rotational alignment $\langle P_2(J' \cdot K) \rangle = -0.49 \sim -0.5$ for both reactions. At $E_{\text{rel}}=0.1 \text{ eV}$, SrBr vibrating within 2.7~3.09 nm is produced with collision time 1.9 ps, and SrI vibrating within 2.8~3.18 nm is produced with 2.2 ps. Ref. X.-X. Zhao, Y.-M. Li, V. W.-K. Wu, Proc. of 10th Chinese Quantum Chem. Nan-Jing, People’s Republic of China.