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Communications

Decay Dynamics of $H_2O(\tilde{A}^1B_1)$: Excitation by two Photon Absorption at 354.6 nm

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Water was photolyzed at 177.3 nm via a two-photon excitation by a frequency-tripled Nd: YAG laser (354.6 nm). The complete product state distribution of the ejected OH product was determined by LIF. The OH is produced in the vibrational ground state exclusively. OH shows a Boltzmann-type rotational distribution with a temperature parameter of about 350 K. No preferred population of Λ - or spin-orbit states was observed.

Introduction

The photodissociation of water is a rather well-studied process and was subject of some recent publications, experimental as well as theoretical ones [1-12]. The H₂O molecule is regarded as a model system for direct photodissociation, because it is simple enough to be treated by ab initio calculations [1-4, 7, 8]. Those calculations on the dissociation process from the $H_2O(\tilde{A}^1B_1)$ state result in the conclusion that a weakly excited OH rotational energy distribution has to be expected. This results from the validity of the Franck-Condon limit for the rotation. The rotational energy distribution is only determined by the internal energy of the dissociating water molecule, scarcely by the photolysis energy [9, 11]. The behaviour of the electronic fine structure distribution is similar to the rotational distribution; it is determined by the Franck-Condon limit. This is only observable in nozzle beam experiments because the thermal motion of the H_2O averages the selectivity of A-state distribution.

Totally different from the rotational excitation is the behaviour of the vibrational degree of freedom of the OH product. Theory predicts a strong dependence of the vibrational excitation on the photolysis wavelength. This is due to a strong coupling of the OH product state with the $H_2O(\tilde{A}^1B_1)$ initial state.

In the present communication we used a photolysis wavelength of 177.3 nm in order to observe the complete product state distribution. Especially the OH vibrational excitation is important for a comparison between theory and the experimental findings. The fragmentation following 193 nm excitation leads to vibrationless products, while at a photolysis wavelength of 157 nm vibrationally excited OH products are generated. However, theory predicts a significantly higher amount of vibrationally excited OH fragments than found in the experiment. At longer photolysis wavelengths it is expected that the OH vibrational excitation will decrease, but the vibrational states should still be populated up to v'' = 2 for a dissociation wavelength of $\lambda = 179.7$ nm [6].

Experimental

The OH product state distribution was determined by the pump and probe technique. The photolysis laser was a Quanta-Ray DCR 1A Nd: YAG equipped with a harmonic generator for frequency tripling, producing the wavelength of 354.6 nm in pulses with an energy of about 60 mJ and a duration of 5 ns. The laser beam was focused into the vacuum chamber with a suprasil lens of 500 mm focal length and had to pass 2 baffles to reduce light scattering. The probe pulses were produced by an excimer pumped dye laser, Lambda Physik LPX 100 and FL 2002 E, running with Sulphorhodamine B, and an external autotracking frequency doubler (inrad). Energy of the probe pulses was about 10 µJ, saturation was prevented by checking the linear dependence of signal intensity on the probe laser power. Laser induced fluorescence was observed with a photomultiplier through an interference filter with maximum transmission at 310 nm. Pump and probe beam counterpropagated collinearly and were focused in the observation area of the PMT. Measurements were carried out at a H₂O pressure of 6 Pa, the pump-probe delay was about 20 ns. The vacuum chamber was evacuated by an oil diffusion pump. The data, LIF signal, pump and probe laser power were collected by SRS boxcar averagers and were stored in a computer (Sicomp PC 32-05).

Results and Discussion

The essential feature of the OH product state distribution can already be seen in the LIF spectrum depicted in Fig. 1. There is no band head of the OH($A^2\Sigma$, v' = 1, $J' \leftarrow X^2\Pi$, v'' = 1, J'') transition observable [13–15], although we tried to excite this transition with pulse energies as high as 100 µJ. Also increasing the H₂O concentration by one order of magnitude did not result in an OH(v'' = 1) signal. From the signal to noise ratio which was better than 100:1 we derive an upper limit for the population in OH(v'' = 1) of 1%.

The excitation wavelength of 177.3 nm, corresponding to a photolysis energy of 56400 cm⁻¹, is reached by a twophoton excitation with the 354.6 nm radiation of a frequency tripled Nd:YAG laser. The square dependence of the signal intensity from the photolysis pulse energy was checked by decreasing the photolysis energy E_p with filters of known



Fig. 1

LIF spectrum of OH photoproducts from the dissociation of H₂O at 354.6 nm via two-photon excitation. There are no lines of the $(v' = 1 \leftarrow v'' = 1)$ transition observable, as indicated by an arrow

transmission. The measurements yielded an exponent of about n = 1.8 for the signal dependence $I \sim E^n$. The process is a non-resonant two-photon absorption because there is no molecular electronic state in H₂O accessible by 354.6 nm [16]. The observed OH vibrational distribution is also an important feature for the excitation mechanism, because it rules out the possibility of a resonant two-photon excitation via extremely high vibrational overtones of the $H_2O(\tilde{X}^1A_1)$ state. If there were an highly excited vibrational state as an intermediate in the dissociation then we would have to expect highly rovibrational excited OH products, which is not observed at all. In a vibrationally mediated photodissociation experiment in which one photon prepares a highly vibrationally excited H₂O and a second photon dissociates the parent it was found that an excitation of the (v_1, v_2, v_3) = (0, 1, 3) H₂O vibrational state results in highly vibrationally excited OH fragments [17].

The observed lack of vibrational excitation is not in accordance with ab initio calculations on the water photodissociation. The calculated photofragment state distribution for a photolysis wavelength of 179.7 nm predicts v'' = 1 and 2 to be populated with a population of approximately 5% in v'' = 1 [6]. The experimental findings are in accordance with the results in a previous paper where we have shown that the OH product vibrational excitation is not as high as predicted from a initio calculations using the H₂O($\tilde{A}^{1}B_{1}$) potential surface [12]. The results of the measurements presented here support our opinion that this H₂O($\tilde{A}^{1}B_{1}$) surface has to be modified by approximately 0.5 eV to explain the deviations between theory and experiment.

Two-photon absorption was already used to study the excitation of H_2O to the \tilde{B} -state, which decays to electronically excited OH(A) that can be analyzed by means of emission spectroscopy [18-21]. For these measurements the frequency-quadrupled output of a Nd:YAG laser was focused into a cell, and the emission of OH(A) was resolved with a monochromator. The rotational distribution of OH(A) peaks at N' near to the energetic limit of $N'_{max} = 9$. With the photolysis energy of 56400 cm⁻¹ only the H₂O(\tilde{A}) state is accessible [16]. $H_2O(\tilde{A})$ decays to electronic ground state OH which was analyzed by LIF. The distinction between resonant and non-resonant two-photon excitation is quite important for it has an influence on the dissocation dynamics due to the time which is necessary for absorption. In the case of the non-resonant process this time is determined by the uncertainty principle for a virtual state is excited. For the resonant absorption this is different, there the lifetime of the intermediate molecular state governs the time delay between the absorption of the first and the second photon. During this time delay there might be an evolution of the systems's wavefunction in the intermediate state that gives rise to an excitation into a different Franck-Condon region in the second step than it would have happened with a single photon of the same energy. For systems without intermediate state the high-power laser induced two-photon absorption is a convenient way of reaching VUV excitation energies with readily available UV wavelengths.

In order to determine the rotational distribution and the Λ -sublevel population we used the line intensities of the Q- and P-branches of the OH spectrum. The product rotational energy distribution is of Boltzmann type with a temperature parameter of 300-350 K. This had to be expected since the OH rotational distribution from water photolysis at 193 nm and 157.6 nm is also thermal and only weakly excited. The rotational distribution is shown in Fig. 2. A-sublevel and spin-state selectivity was not observed and could not be expected since we performed a static gas experiment [9, 11].



Fig. 2

Boltzmann plot of the rotational state distribution of the OH photofragments. Q_1 : \diamond , Q_2 : \triangle , P_1 : \times , P_2 ; ∇

The results presented here partly support the common opinion on the photodissociation of water in its first absorption band. There is a low rotational excitation of the OH product, very much alike the distributions obtained in the 193 nm and 157.6 nm photolyses [11,12]. This is in good agreement with the presumed validity of the Franck-Condon limit for this part of the fragmentation process. The product vibrational distribution shows a contrary behaviour, it is strongly dependent on the excitation energy. Clearly, this is a result of the strong coupling between the excited state $H_2O(\tilde{A}^1B_1)$ and the product states. For we have determined significant deviations from the theoretical calculations as far as the vibrational distribution is concerned we would like to mention that these results are consistent with our earlier measurements on the H_2O photodissociation at 157.6 nm.

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- Dielectric Relaxation of N-Cyano Substituted Morpholine, Piperidine and Pyrrolidine

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Dielectrics. Solutions

The dynamic dielectric properties of the title substances are measured at 20°C at frequencies up to 72 GHz in the pure liquid state and in mixtures (x = 0.4-1) with benzene and tetrachloromethane. Rotational tumbling motion of single (non-associated) molecules is likely to be the main relaxation process. Peculiarities are found with two out of the six systems, namely mixtures of cyanopiperidine and cyanopyrrolidine with tetrachloromethane. These are discussed as possibly due to a concentration dependent conformational equilibrium.

Introduction

In a previous paper [1] we reported on the dynamic dielectric properties of morpholine and some of its derivatives, among which N-cyanomorpholine seemed to indicate a somewhat special relaxation behaviour as pure liquid and in mixtures with benzene. The question as to whether or not there are actually peculiarities stimulated the present investigation of some comparable systems. It is again concerned with N-cyanomorpholine (CyMo) and further with two related heterocyclic compounds of comparable molecular size and dipole moment, namely N-cyanopiperidine (CyPi) and

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N-cyanopyrrolidine (CyPy). To our knowledge the dynamic dielectric properties of the latter liquids have not yet been investigated. This communication describes the relaxation behaviour of the three substances in the pure liquid state and in semidilute mixtures with benzene or tetrachloromethane which are regarded in order to eventually discern specific self or hetero-interaction effects.

Experimental

The complex permittivity spectra of the liquids were obtained at 20 °C over a frequency range between some 10 MHz and 72 GHz, employing different fixed frequency apparatus. Primarily the imaginary part $\varepsilon''(\omega)$ of the permittivity as already corrected for the conductivity contribution was considered. Its uncertainty is a few percent at all frequencies. Viscosities were measured with an Ostwald viscosimeter.

Chemicals from Aldrich and Merck were used as obtained.

Results

Already a cursory examination of the $\varepsilon''(\omega)$ data shows that for all the present systems the absorption curves are nearly of Debye character, being slightly broadened on the high frequency side. They can be fitted by a sum of two Debye type spectral components C_{i} , viz.

$$\varepsilon''(\omega) = \sum_{i,2} S_i \frac{\tau_i \omega_i}{1 + \tau_i^2 \omega_i^2}, \qquad (1)$$

where component C_1 is the principal one, while C_2 denotes a minor high frequency component. The results will be given in terms of the parameters τ_i (relaxation time) and S_i (relaxation strength). Results