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REMPI-TOF studies of the HF dimer

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Abstract

Resonance-enhanced multiphoton ionisation and time-of-flight mass spectra analysis of jet-cooled HF–argon mixtures are presented. Two-photon resonance transitions in the HF dimer, $(HF)_2$, are observed for the first time. Simulation calculations reveal transitions to a Rydberg state and allow determination of energy parameters for the excited state dimer. The process of excitation is discussed.

Keywords: Hydrogen bonds; REMPI; dimer; multiphoton; ionization; Laser spectroscopy; jet cooling; simulations

1. Introduction

Hydrogen fluoride forms the strongest hydrogen bond ($1038\ cm^{-1}$)[1] in the series of the hydrogen halides. Therefore, the system has become a popular model for investigations of hydrogen bonds. The HF dimer has been extensively investigated both experimentally[1–7] and theoretically [4,8,9,10], whereas properties of larger HF oligomers mostly have been predicted theoretically [4,11,12] but to a much lesser extent experimentally [13]. Microwave [2] and infrared [3,1,4,6] spectra analysis as well as laser-induced fluorescence studies [5,7] have revealed accurate spectroscopic and structural parameters for the dimer. In studies of the HF, dimer emphasis has been laid on energy and structure properties of the ground electronic state whereas no studies have been performed on excited states. As a matter of fact even very limited experimental studies have been performed on electronically excited states of the monomer [14]. This could partly be due to the fact that absorption due to electronic transitions appears in the VUV region [15,16] making experimental studies unfavourable. Furthermore, several early reports on high-energy interactions of HF have revealed highly anomalous and aggressive behaviour of the gas [17] suggesting that a great care needs to be taken in its handling.

For some time, REMPI studies of the hydrogen halide monomers, HX; X = Cl, Br and I, have been performed in our laboratory emphasizing characterization of Rydberg and ion-pair excited states based on the simulation calculations for two- and three-photon resonance excitation processes [18–25]. In this paper, we report resonance-enhanced multiphoton ionisation of jet-cooled hydrogen fluoride gas diluted in argon followed by TOF mass analysis. Simulation analysis of recorded spectra revealed two-photon absorption in the HF dimer due to transitions to a Rydberg state and allowed characterization of energy and spectroscopic parameters.

2. Experimental

Resonance-enhanced multiphoton ionisation (REMPI) of jet-cooled HF gas in argon was performed in the middle of an ionisation chamber. Ions were directed into a time-of flight tube and detected by MCP plates to record ion yield as a function of flight time and/or as a function of laser radiation wavenumber.

Tunable excitation radiation was generated by an Excimer laser-pumped dye laser system, using a Lambda Physik COMPex 205 Excimer laser and a Lumonics Hyperdye 300 laser. A C-460 dye was used and the energy per pulse was about 5 mJ. The repetition rate was 10 Hz. The bandwidth of the dye laser beam was about $0.05\ cm^{-1}$. The radiation was focused into an ionisation chamber between a repeller and an extractor separated by 19 mm. Gas samples, made by mixing HF gas from Schuchardt and argon on a vacuum line, typically in the ratio 1:3, were pumped through a 200 μm pulsed nozzle from a typical total backing pressure of about 3 bar into the ionisation chamber, which was held at lower than about 5×10^{-6} mbar pressure during experiments. The distance between the nozzle and the centre between the repeller and the extractor was about 5 cm. The nozzle was held open for about 180 μs

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and the LASER beam was typically fired about 450 μs after opening the nozzle. Ions were extracted into a 70-cm long time-of-flight tube and focused with an electric lens onto a MCP plate detector. Voltage outputs as a function of flight time were fed into a LeCroy 9310A, 400 MHz storage oscilloscope. Average voltage outputs for a fixed number of laser pulses were evaluated and recorded on a computer to get mass spectra. Either mass peak heights or integrals were measured and averaged for fixed number of laser pulses as a function of laser radiation wavenumbers to obtain (2+1)REMPI-TOF spectra. Typically spectral points were obtained by averaging over 100 pulses.

Care was taken to prevent power broadening due to ac-Stark effects by minimizing the laser power. Wavelength calibration was achieved by recording iodine atomic lines or by measurements and comparison of the strongest hydrogen chloride rotational lines with those reported by Green et al. [26]. The accuracy of the calibration was found to be about $\pm$ 1.0 cm^{-1} on a two-photon wavenumber scale. Care was taken to correct for possible drifts in signal intensities during long scans. Furthermore, the effect of varying laser power was corrected by dividing the measured intensity by the power squared.

3. Results and analysis

The wavenumber range, where (2+1)REMPI spectra of HF will be observed, is determined by the molecular ionisation energy (IE = 16.039 eV/$\overline{\text{IE}}$ = 129,360 cm^{-1}) [14]. The minimum and maximum laser wavenumbers ($\tilde{\nu}_{laser}$) for (2+1)REMPI correspond to the photon energies which equal one-third and half of the ionisation energy, respectively. Therefore, the excitation wavenumbers range ($\tilde{\nu}_{exc} = 2\tilde{\nu}_{laser}$) for (2+1)REMPI is

$$86241 < \tilde{\nu}_{exc}/cm^{-1} < 129360$$

Fig. 1 shows mass spectra as ion yields vs flight time for the two-photon resonance excitation wavenumber range 86,612–86,626 cm^{-1}. These spectra were recorded after flushing the system with HF–argon mixtures for several hours to eliminate signals from possible impurities on the line, which is known to be important, due to the aggressive nature of HF(g) [17]. Only one mass at about 11.5 μs flight time, which corresponds to a mass of about 19–21 amu, was detected. This we believe that is HF^+ or alternatively H_2F^+ which is isoelectronic to H_2O and lower in energy than HF^+ [27]. Experimental REMPI spectrum obtained by recording the integrated mass spectra as a function of excitation wavenumbers is shown at the top of Fig. 2. This must be a rovibrational band due to a two-photon resonance excitation followed by a one-photon ionisation in hydrogen fluoride.

The observed, high-frequency, partly resolved rotational structure of the band could not be reproduced by simulation calculations assuming rotational structure of the ground state of HF ($B_{v''=0} = 20.5567$) [14] whereas it could easily be simulated by assuming the ground state to be the dimer $(HF)_2$, with two orders of magnitude smaller rotational constant ($\bar{B}_{(0,0)} =$ 0.21666 cm^{-1}) [3] as seen in Fig. 2. Furthermore, the signal enhanced profoundly with jet cooling, hence increasing cluster formations, as the backing pressure was enlarged. We, therefore, conclude that the signal originates from resonance excitation in the HF dimer. Since only HF^+ or H_2F^+ ions but no $(HF)_2^+$ ions were detected, dissociation of a neutral intermediate state or the dimer ion must occur in the excitation process.

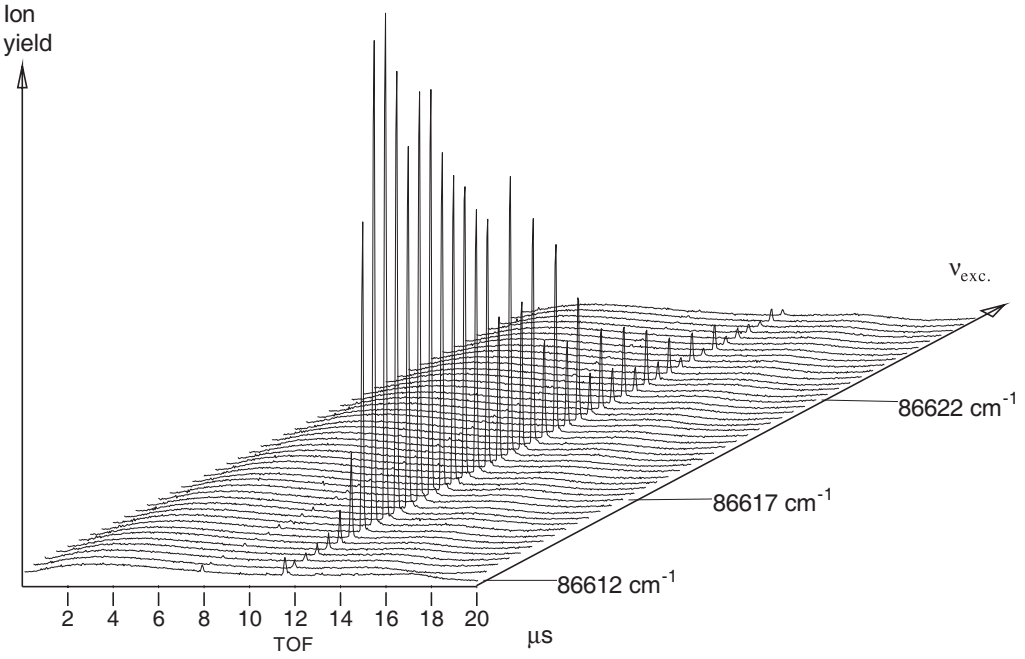

Fig. 1. Jet-cooled HF(g)–argon (1:3) sample mass spectra recorded in a REMPI-TOF mass spectrometer (ion yield vs time-of-flight (μs)) as a function of two-photon laser wavenumber excitation (86,612–86,626 cm^{-1}).