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High Resolution FTIR Overtone Spectra and Hydrogen Bond Dissociation Dynamics in $(HF)_2$**

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Abstract: The first successful observation of the HF-stretching overtone spectra assigned to the hydrogen bonded HF-dimer in the near infrared region from 7100 to 8100 cm^{-1} is reported. Partially pressure broadened bands with linewidths of 0.16 cm^{-1} and less were found, which imply vibrational predissociation lifetimes of more than 30 ps. This result is discussed in terms of the efficient vibrationally adiabatic decoupling of the high frequency vibrations and the resulting limitations of quasi-equilibrium theories of unimolecular reactions.

The dynamics of hydrogen bond formation and breaking is of fundamental importance for the understanding of biological processes and of condensation and evaporation phenomena in hydrogen bonded liquids[1]. The hydrogen bonds in the HF-dimer and in liquid HF presumably represent the simplest model system. Surprisingly, even in this simple system the primary kinetic processes are poorly understood. One approach to a deeper understanding is provided by high resolution spectroscopic studies of the predissociating HF-dimer. An early report has been given by *Klemperer*[2], and more recently *Pine* et al.[3] and *DeLeon* and *Muenter*[4] have reported linewidth measurements in the range of the HF fundamental transitions around 3900 cm^{-1}. The situation is sketched in Fig. 1, from which one sees that already the energy of the HF fundamental stretching transition largely exceeds the $(HF)_2$ hydrogen bond dissociation energy of about $\Delta U_0^0 = (hc)$ 1800 cm^{-1} (see, however,[10]). *Pine* et al. have inferred a predissociation lifetime of 800 ps when exciting in the region of the bonded HF absorption[3]. This contrasts with much longer lifetimes estimated by some theoretical models[5,6], although the difficulties seem to have been largely resolved recently[7]. However, it has also been suggested that semiclassical equilibrium statistical theories might provide an interesting description[8].

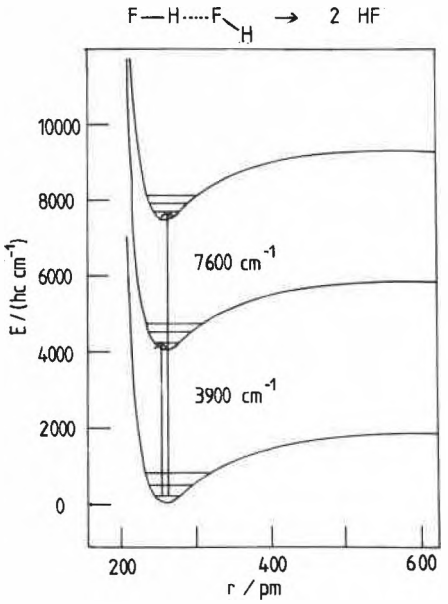

Fig. 1. Schematic drawing of vibrationally adiabatic $(HF)_2$ channel potentials showing quasibound states and the fundamental and overtone transitions of the HF stretching vibrations. Predissociation occurs by transferring HF stretching energy into the low frequency modes including the reaction coordinate.

Experimentally the most pressing questions concerning the dynamics of hydrogen bond breaking after local HF excitation concern clearly the observation of fine structure, if any, in the higher overtones of the HF stretching vibrations in the HF-dimer. Because of the much smaller signal compared to the fundamental absorption no previous work has been published on any of the overtones. We report here preliminary results concerning the fine structure of the first overtone region. These results are of great importance for the theoretical understanding of the dissociation. One should see also the relationship to vibrational relaxation via dimer formation[9] and the condensation process in molecular beams[10]. The interaction potential of two HF molecules has also been a challenge to quantum chemists[11] (a more detailed account of the literature will be given elsewhere[12]).

Experimental

The spectra have been recorded on our BOMEM DA 002 interferometric Fourier Transform spectrometer system allowing for a maximum apodized resolution of 0.004 cm^{-1}. Because of pressure broadening largely exceeding this value in the experiments reported here, we used lower resolutions in practice, avoiding however instrument limited bandwidths (note that also the Doppler width of $(HF)_2$ lines around 7600 cm^{-1} exceeds 0.014 cm^{-1}). Although our experiments have covered the whole IR up to the visible, only the range of the $v = 2$ overtone absorption will be discussed. The HF dimer was created under equilibrium conditions between 250 and 300 K and pressures between 1 and 50 kPa in two home-built thermostated cells with optical path lengths of 4 m and 10 m. The temperature was controlled to within about ±1 K. The HF was obtained from Matheson and also produced in our laboratory from CaF_2 and H_2SO_4 at about 500 K. There did not seem to be appreciable impurities other than air and minor amounts of water.

Results and Discussion

Fig. 2 shows an overview of the $(HF)_n$ vapour spectrum in the HF stretching overtone range. The monomer spectrum is obvious from its P–R structure. The broad red shifted absorption arises from various polymers ($n > 2$). The hardly visible substructure between the monomer P–R lines arises from the dimer. This is shown in more detail in Fig. 3. The structures are easily visible and Fig. 3b shows an expanded portion of the fine structure of the dimer spectrum. These structures are assigned to HF-dimer absorption on the basis of the following evidence: (i) The strength of the absorption is in rough agreement with predictions of the $(HF)_n$ equilibria[13]. (ii) Impurity absorptions can be excluded because of various sample preparations used in the experiments leading always to the same results. The HF-H_2O impurity absorption could be assigned under some conditions, when it occurs. (iii) The fine structure of the absorption shows close similarities with the fine structure of the fundamental transitions in the dimer. Points (i) and (iii) are strong evidence in favour of the dimer assignment as compared to higher polymers. The correlation of the line strengths with the calculated[13] trimer partial pressure, for instance, is poor. It must be noted, however, that the thermodynamics of $(HF)_n$ is still under debate[10,13]. However, we have obtained a preliminary K-assignment for a

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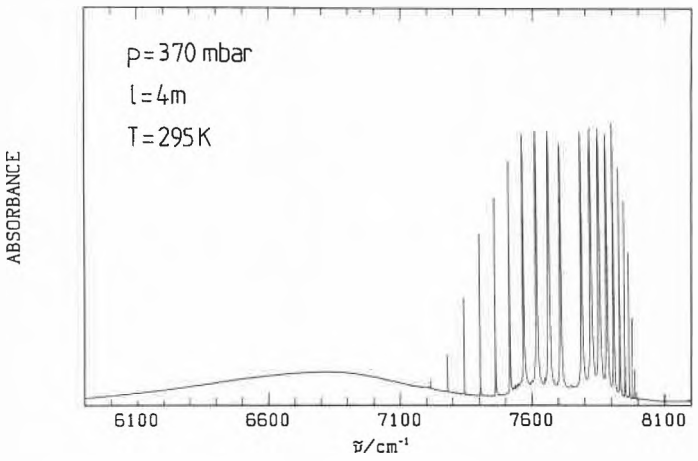

Fig. 2. Overview spectrum in the first overtone region of HF-polymers ($p = 37$ kPa, $l = 4$ m, room temperature).

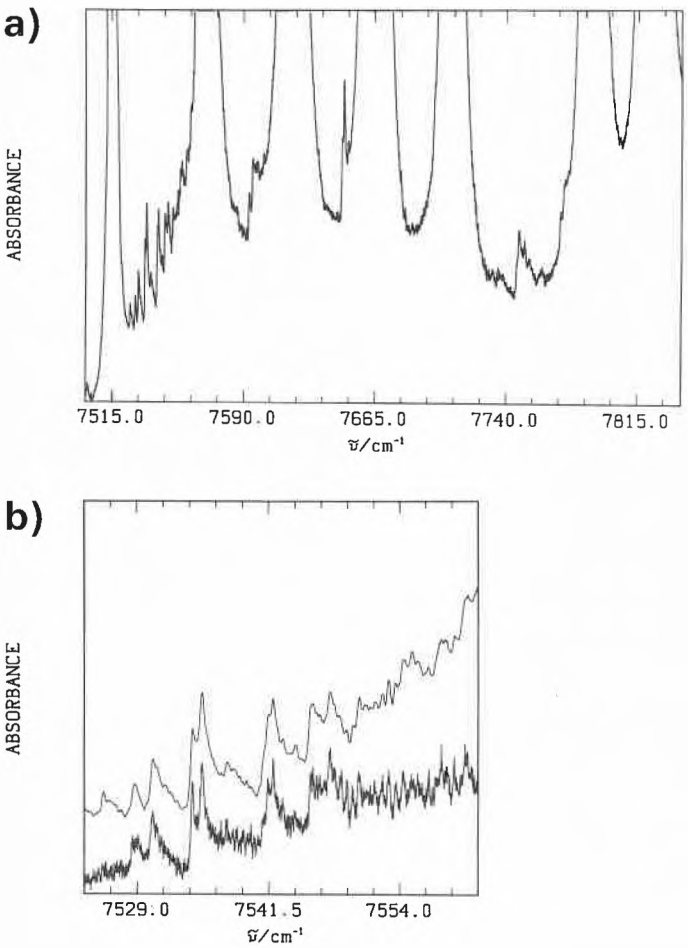

Fig. 3. a) Detail of Fig. 2 showing the fine structure in the spectrum of the HF-dimer. – b) Fine structure in the 7500 cm^{-1} region at two resolutions (upper trace as in Fig. 3a, lower trace: $p = 14$ kPa, $l = 10$ m, $T = 265$ K, resolution 0.025 cm^{-1}).

number of features occurring in the 7100 to 8100 cm^{-1} range, with rotational constants being consistent with the well known values from the ground state[3,12]. Even, if the quantum state labeling and thus the band center assignment still may shift, this is practically conclusive evidence in favour of assigning the fine structure to dimer absorption.

$(HF)_2$ has two high frequency stretching vibrations, one related to the H-atom involved in the hydrogen bond (see Fig. 1) with a fundamental frequency ν_2 at 3868 cm^{-1}, the other, ν_1, at 3931 cm^{-1}. Both are split by the tunneling between the two possible structures of $(HF)_2$ (by 0.9 and 0.44 cm^{-1}, respectively). For the overtone region three possible bands result, with $v_1 = 2$, $v_2 = 2$, and $v_1 = v_2 = 1$. A first estimate from our preliminary assignments places the $v_1 = 2$ band center near 7679 cm^{-1}. If this is confirmed by a more detailed analysis one has thus $\omega_e^{(1)} = 4113$ cm^{-1} and $\omega_e x_e^{(1)} = 91$ cm^{-1}. Similarly for $v_2 = 2$ a tentative band center would be 7542 cm^{-1} giving $\omega_e^{(2)} = 4063$ cm^{-1} and $\omega_e x_e^{(2)} = 97.5$ cm^{-1}. These values may be compared to the free HF stretching vibration[14] with $\omega_e = 4138.32$ cm^{-1} and $\omega_e x_e = 89.88$ cm^{-1}, and the differences appear to be reasonable. Of course, the tunneling splitting is observed also in the overtone of the dimer. Work is in progress to confirm these constants by a more complete rotational analysis of the spectra, which may change somewhat the values given above.

A most significant result which is independent of the precise location of the band centers concerns the observation of fine structure with widths of the order of 0.1 cm^{-1} for a molecule having about four times the energy needed for dissociation. The pressure broadening coefficient could be determined for some bands to be near 13 cm^{-1}/MPa. With experimental pressures around 0.01 MPa and more, the measured widths may thus be largely due to pressure broadening and provide only an upper limit for predissociation widths. Even so, a typical value of 0.16 cm^{-1} for the width of some of the sharper features implies dissociation lifetimes of more than 30 ps. The long lifetimes seem to be qualitatively consistent with the model of reference[7]. They are certainly inconsistent with equilibrium statistical theories of unimolecular reactions[15–17]. Accurate estimates for lifetimes and densities of states are not possible, as the dimer is highly nonrigid and none of the low frequency fundamentals is known accurately. However, even very cautious estimates would give lifetimes at least an order of magnitude lower. The breakdown of the equilibrium statistical theory of unimolecular reactions in this case is not unexpected[18] and can be related to the high degree of adiabatic separation of the HF-stretching motion from the low frequency modes around 500 cm^{-1} and less. We have demonstrated before, how the adiabatic separation may have profound influence on vibrational redistribution[19], of which vibrational predissociation is just a limiting case. The rate of vibrational redistribution has to be taken into account explicitly in $(HF)_2$. Experiments at higher resolution will provide more reliable predissociation linewidths. The present results, proving the location of definite fine structures in the overtone region, provide an essential first step towards this goal.

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