

Vibrational Predissociation in Hydrogen Bonded Dimers: The Case of (HF)₂ and its Isotopomers

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Dedicated to Wilfred van Gunsteren on the occasion of his 60th birthday

Abstract: We use the dimer (HF...HF) as a model system to understand the dynamics in hydrogen-bonded systems. This particularly simple system has been widely used both in experimental and theoretical studies. Here we focus on the remarkable mode selectivity in vibrational predissociation processes which occur on time scales of picoseconds to nanoseconds. We have performed classical molecular dynamics (MD) calculations on the six-dimensional SO-3 potential energy surface (PES) of (HF)₂^[1] to estimate absorption spectra and predissociation lifetimes τ_{PD} for various initial vibrational excitations involving HF stretching. Our calculations can qualitatively reproduce the mode selectivity in τ_{PD} observed experimentally: Excitations involving the 'hydrogen-bonded' HF stretching mode give rise to shorter τ_{PD} than those involving the 'free' HF stretching mode. Besides results concerning the HF dimer, this study offers the opportunity to check to what extent classical MD calculations on an accurate and realistic potential are suitable to study dynamical properties in such a molecular system.

Keywords: Classical molecular dynamics · Dimer (HF)₂ · IR-spectroscopy · Isotopes · Unimolecular reaction dynamics ·

1. Introduction

In theoretical studies of chemical reaction dynamics restricting attention to fully dynamical approaches one has the choice among several possibilities of treating the nuclear degrees of freedom, if one accepts as starting point the electronically adiabatic

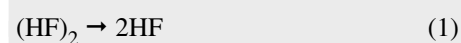
(Born-Oppenheimer^[2]) approximation at least for the processes in the electronic ground state.

- i) One can treat the nuclear motion by classical dynamics following Newton's or Hamilton's equations of motion.^[3]
- ii) One can treat the motion 'exactly' fully quantum mechanically.^[4]
- iii) One can use semiclassical theory following essentially the development of the 'old' quantum theory of Bohr and Sommerfeld^[5] or
- iv) one can also treat some nuclear degrees of freedom by quantum mechanics, while some other degrees of freedom are treated by classical mechanics (sometimes called the 'mixed quantum-classical approach').

In the treatment of large molecular systems such as biomolecular dynamics the purely classical approach has been extremely fruitful over the last decades, to a substantial extent also related to developments of potential models and numerical methods in the work of W. van Gunsteren and his associates.^[6–8]

Nevertheless, there have been relatively few investigations, where for an experimen-

tally well studied system for which also accurate potential hypersurfaces are known, detailed comparisons of the effect of the various dynamical approximations have been made. One such example is the bimolecular H + H₂ reaction and its isotopomeric variants^[9–13] where quantum effects are clearly very important, given that only very light atoms are involved. A more interesting case would be a system which contains heavy atoms together with hydrogen, where the reaction process studied concerns the motion of the heavy atoms and the light atoms are to some extent 'spectators' in the process, as is often the case in biomolecular dynamics. We have chosen here the vibrational predissociation reaction (1) of the dimer (HF)₂



for such a benchmark study. Such a system can also be used as a test case for statistical theories of scattering in complex forming reactions and vibrational predissociation.^[14,15]

(HF)₂ is among the simplest hydrogen-bonded dimers. It has been frequently used

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as prototype system to understand hydrogen bond dynamics. In particular, its simplicity allows for investigations by high resolution rotational-vibrational spectroscopy.^[16–36] One interesting property is the dynamics in vibrational predissociation: Vibrational predissociation lifetimes τ_{PD} of the dimer $(\text{HF})_2$ were measured using sub-Doppler resolution molecular beam spectroscopy for excitations of the HF stretching fundamental vibrations.^[17,18,20,22] These experiments have revealed that τ_{PD} is highly mode specific: the excitation of one quantum of the hydrogen bonded HF stretching ν_{b} vibration (Fig. 1) gives rise to a predissociation lifetime more than 20 times shorter than that of the ‘free’ non hydrogen-bonded HF stretching ν_{f} vibration. The initially excited states with $\nu_{\text{b}} = 1$ or $\nu_{\text{f}} = 1$ are the two components of the so-called $N = 1$ dyad. The polyad quantum number $N = \nu_{\text{b}} + \nu_{\text{f}}$ generally labels states with nearly the same energy, where ν_{b} indicates the number of quanta in the hydrogen bonded HF stretching mode and ν_{f} the number of quanta in the ‘free’ HF stretching mode. The predissociation spectra in the $N = 2$ triad were observed by FTIR-spectroscopy^[23] and by supersonic jet diode laser absorption and cw-laser spectroscopy.^[26,34,35] This polyad offers three possibilities of distributing the quanta among the two stretching modes (ν_{b} , ν_{f}). The lowest polyad member 2_1 corresponds about to $(\nu_{\text{b}} = 2, \nu_{\text{f}} = 0)$ with experimental band center at $\tilde{\nu}_0 = 7550.355 \text{ cm}^{-1}$.^[34,35] The next higher polyad member 2_2 corresponds about to $(\nu_{\text{b}} = 0, \nu_{\text{f}} = 2)$, with experimental band center at $7711.3796 \text{ cm}^{-1}$.^[23,26,34,35] and the highest component 2_3 corresponds to $(\nu_{\text{b}} = 1, \nu_{\text{f}} = 1)$ with band center at 7795.0 cm^{-1} .^[35,37] The mode selectivity in τ_{PD} is preserved in the $N = 2$ triad between 7500 and 7800 cm^{-1} , *i.e.* more than seven times the dissociation threshold for breaking the hydrogen bond ($D_0 = 1062 \text{ cm}^{-1}$). Already experiments by FTIR spectroscopy have shown that they exhibit a mode selective, highly non-statistical, non-RRKM (Rice-Ramsperger-Kassel-Marcus) behaviour.^[23] More recently, experiments using very high resolution cw-laser cavity ring-down spectroscopy^[34] have shown that the $2_1 \equiv (\nu_{\text{b}} = 2, \nu_{\text{f}} = 0)$ excitation gives rise to a predissociation lifetime by far shorter than the $2_2 \equiv (\nu_{\text{b}} = 0, \nu_{\text{f}} = 2)$ excitation, while the $2_3 \equiv (\nu_{\text{b}} = 1, \nu_{\text{f}} = 1)$ excitation exhibits an intermediate behaviour.^[34,35,37,38] τ_{PD} have also been measured in the $N = 3$ polyad and display similar mode selectivity as in the lower polyads.^[39,40]

Concerning theoretical studies, the small size of the system has allowed the construction of increasingly accurate electronic potential energy hypersurfaces (PES).^[1,24,41–46] Halberstadt *et al.*^[47] calculated the predissociation lifetime for the ν_{b} excitation in a three-dimensional quantum dynamics study.

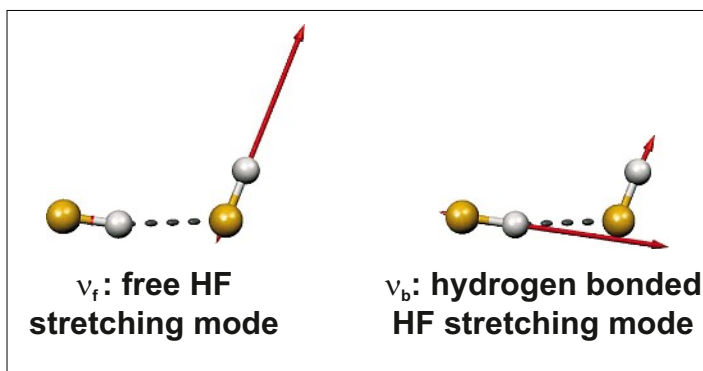


Fig. 1. The two HF stretching vibrational normal modes of the dimer $(\text{HF})_2$ on the SO-3 surface. The arrows indicate the relative amplitude of motion for each atom along the normal mode.

In contrast to many previous models their results are in qualitative agreement with experiments.^[19,23,34,35] Later on, Bacic, Zhang and their co-workers have used a quantum mechanical golden rule treatment based on four-dimensional calculations employing several PES^[48–50] including in particular the SQSBDE surface.^[24] They have estimated τ_{PD} for various states and underlined that the vibrational predissociation dynamics of the HF dimer is very sensitive to details of the PES. Since then, a new fully six-dimensional analytical PES has been established in our group.^[1] This so-called SO-3 PES (for semiempirical-overtone adjusted) is up to now the best available pair potential empirically refined on experimental data for a four-atom hydrogen bonded system.

In this work, we propose to use *classical* molecular dynamics on the SO-3 PES to compute trajectories and vibrational predissociation lifetimes of the dimer $(\text{HF})_2$. This is to our knowledge the first study where such calculations are performed on a realistic potential of near to spectroscopic accuracy. Our goal is not to predict predissociation lifetimes of $(\text{HF})_2$ with the best available accuracy. We rather want to take the experimental and theoretical knowledge on the vibrational predissociation of $(\text{HF})_2$ into account in order to use it as a benchmark: This approach offers the opportunity to check if classical MD calculations on an accurate potential are suitable to study certain dynamical properties. Such a study can provide insights for estimating the merits and limitations of classical MD calculations, widely used in the case of larger systems, for which potentials are necessarily of lower accuracy.

2. Methods Used in the Classical Trajectory Model Calculations

For the MD calculations, Newton’s equations of motion were solved by means of a Verlet-adapted so called half-step leapfrog algorithm.^[51] To reduce the compu-

tational time evaluating the forces derived from the potential, we used a multiple time step method (see ref. [51] and citations therein) which we have adapted to our problem. A time step δt of $2.3 \cdot 10^{-18} \text{ s}$ was used for all simulations in order to properly reproduce HF stretching oscillations. The following atomic masses were used for the simulations: $m_{\text{H}} = 1.0078250 \text{ u}$, $m_{\text{F}} = 18.9984032 \text{ u}$, and $m_{\text{D}} = 2.014101779 \text{ u}$ (see also [52]). The following initial excitations were investigated: $(\nu_{\text{b}} = 1, \nu_{\text{f}} = 0)$; $(\nu_{\text{b}} = 0, \nu_{\text{f}} = 1)$; $(\nu_{\text{b}} = 2, \nu_{\text{f}} = 0)$; $(\nu_{\text{b}} = 1, \nu_{\text{f}} = 1)$; $(\nu_{\text{b}} = 0, \nu_{\text{f}} = 2)$; $(\nu_{\text{b}} = 3, \nu_{\text{f}} = 0)$; $(\nu_{\text{b}} = 0, \nu_{\text{f}} = 3)$. For each excitation of the $N = 2$ triad, more than 60 simulation runs have been investigated, with different starting configurations, whereas for the excitations of the $N = 3$ polyad more than 35 starting configurations have been investigated, and for $N = 1$ dyad excitations, more than 20. A starting configuration is obtained by a displacement of the atoms from their equilibrium positions along a linear combination of the six normal modes, the energy of which reproduces the anharmonic zero point energy (the i -th normal mode roughly contributes for $hc \tilde{\nu}_i/2$ to the total energy of the dimer) and in addition an extension along the normal mode, which reproduces the anharmonic energy of the chosen excitation. The difference between two starting configurations of the same excitation results from different phases of the six normal modes. With this simple model, the initial state of the dimer at $t = 0$ has only potential energy. For more details of the method and more extensive calculations we refer to a forthcoming paper.^[53]

3. Results and Discussion

We illustrate here first with an example some general characteristics observed in all simulations. Fig. 2 shows the time-dependence of four geometrical parameters for a single trajectory with an initial excitation $(\nu_{\text{b}} = 0, \nu_{\text{f}} = 2)$: the H–F bond length of the

initially free (r_1) and the initially bonded (r_2) monomers, the F...F distance (R_{FF}), and the angle between the initially bonded monomer and the FF axis (θ_2). As expected, at the beginning of the simulation, the excited HF bond length r_1 exhibits the largest amplitude motion. The other coordinates show little amplitude. After about 400 ps, θ_2 oscillates between 180° and 0° and θ_1 (the corresponding angle for the free monomer, not shown here) oscillates in a complementary fashion between 0° and 180° at the same time: The two monomers start exchanging their H-bond donor/acceptor character following the schematic process indicated in Fig. 3. This process quantum mechanically occurs by above barrier tunnelling^[34,54] while it is purely classical in the present model. The energy located in the initially free HF monomer is during

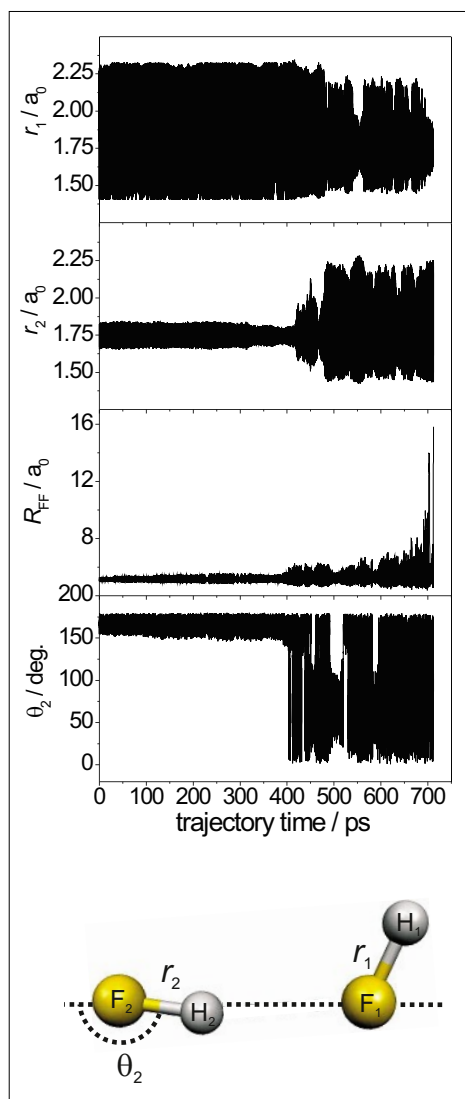


Fig. 2. Top: Time dependent geometrical parameters of (HF)₂ for an initial excitation ($v_b = 0$, $v_f = 2$). Bottom: the four geometrical parameters of interest: r_1 is the HF bond length of the initially free and r_2 of the bonded monomer, R_{FF} is the distance between the two fluorine atoms and θ_2 is the angle between the initially bonded monomer and the FF axis.

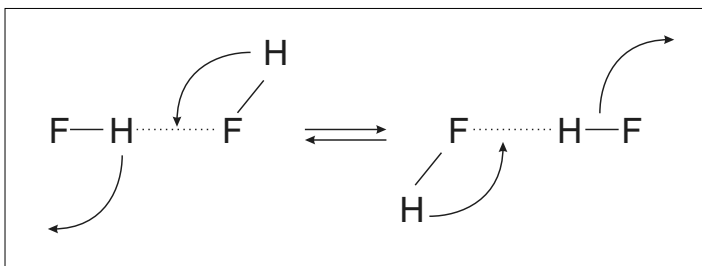


Fig. 3. Hydrogen bond switching rearrangement process in (HF)₂.

this process partially transferred to the initially bonded monomer. The F...F distance also starts oscillating with larger and larger amplitude until the dimer dissociates after about 700 ps. Averaging over many trajectories of this kind one obtains an average lifetime for a given initial excitation.

The resulting average predissociation lifetimes τ_{PD} for all excitations are summarised in Table 1; Experimental and computed values from previous work are indicated for comparison. We have performed a few calculations for the ($v_b = 1$, $v_f = 0$) excitation of the $N = 1$ dyad using our classical approach on the SQSBDE potential. The results can be directly compared to quantum dynamical results on the SQSBDE potential.^[48,50] This provides an estimate of the error on the computed τ_{PD} due to the classical approach itself. If the computed τ_{PD} with the quantum approach was already too long (around 3 ns) compared to the experimental results (480 ps), which the authors attributed to the insufficient quality of this potential (of 1990/91^[24,44]), none of the 20 simulation runs we have propagated leads to τ_{PD} shorter than 9900 ps. Our averaged value with the classical approach is definitely off by at least one order of magnitude.

On the other hand, calculations using the same classical approach on the more accurate SO-3 potential provide interesting results. The lifetimes are shorter than the results for the SQSBDE potential by at least a factor of 4 (see values in Table 1). The shorter τ_{PD} for the v_b excitation, closer to the experimental values, obtained with our approach indicates that effects from changes in the potential are almost as large as quantum effects. If one scales down the quantum result on the SQSBDE potential by a factor of 4 as found in classical calculations (a somewhat bold procedure) it comes close to the experimental result. Our preliminary results concerning the mixed dimers HF-DF and DF-HF (indicated in Table 1) are in agreement with the general trend observed experimentally, but have to be confirmed.

Concerning the region of the $N = 2$ polyad, the order of magnitude and the mode-selectivity of predissociation lifetimes for the three possible excitations agree qualitatively with experimental data: The initial

excitation ($v_b = 2$, $v_f = 0$) leads to shorter predissociation lifetime than the ($v_b = 0$, $v_f = 2$) excitation, and the calculated τ_{PD} for the ($v_b = 1$, $v_f = 1$) excitation exhibits an intermediate behaviour (see values in the Table). We conclude that the classical approach on the more accurate PES works reasonably well at least qualitatively.

Nevertheless, looking at the results in more detail, one finds that for excitations involving the v_b stretching vibration only, our computed predissociation lifetimes are too long by a factor of about 6 compared to the experimental values. This was also the case for the quantum calculations.^[50] The authors argued that the decay width used in their calculations is highly sensitive to the quality of the PES. Actually our results seem to agree with their explanation since we obtain lifetimes significantly shorter with the more realistic SO-3 surface than with the SQSBDE surface. To definitely conclude and quantify the effect of the quality of the potential energy surface, one should also compute τ_{PD} with the quantum approach on the SO-3 potential.

Finally, for the excitations involving the v_f stretching vibration, the root mean square deviations of the τ_{PD} -mean value can be sometimes quite high. For instance the excitation ($v_b = 0$, $v_f = 2$), more than 25% of our starting configurations yield predissociation lifetimes significantly longer than the mean value (by a factor 2 to 4), forming a kind of 'sub-ensemble'; such a behaviour was not observed for the $2v_b$ excitation. We could not find any simple correlation, between the long lifetimes and the starting configurations used in our calculations. We assume that the contribution of the low-frequency modes *via* zero point energy can play a crucial role. The higher sensitivity of the results with the starting configurations for ($v_b = 0$, $v_f = 2$) to low frequency mode contribution than those for ($v_b = 2$, $v_f = 0$) is another indication that this approach can reproduce the mode selectivity from a qualitative point of view only.

To summarize, the goal of this study is to estimate to what extent a classical approach is suitable to predict a detailed dynamical property in a simple molecular system. We have used the vibrational predissociation of (HF)₂ as a probe. Our preliminary calculations on the 'rather good' SQSBDE

Table 1: Experimental ($\tau_{\text{PD}}^{\text{exp}}$) and calculated ($\tau_{\text{PD}}^{\text{calc}}$) predissociation lifetimes of the HF dimer. All the excitations have been computed for $(\text{HF})_2$ (except the ν_b excitation where few calculations for the mixed isotopomers are shown). The PES used for the calculations as well as the number of simulations used for the evaluation of the average value are indicated.

Excitation	$\tau_{\text{PD}}^{\text{exp}}$ / ps	$\tau_{\text{PD}}^{\text{calc}}$ / ps	PES	# Simul.	Reference
$1_1 \equiv (\nu_b = 1, \nu_t = 0)$ ($\text{HF})_2$ (3870 cm^{-1})	480 (40) ^a				[22]
		3000	SQSBDE ^[24]		[48]
		3120/3300	SQSBDE ^[24]		[50]
		>9900	SQSBDE ^[24]	23	This work
		2520(1050) ^a	SO-3 ^[1]	23	This work
HF-DF (2840 cm^{-1})	1300 (40) ^a				[31]
		7600	SQSBDE ^[24]		[55]
		>11700	SO-3 ^[1]	5	This work
DF-HF (3870 cm^{-1})	570 (80) ^a				[31]
		4000	SQSBDE ^[24]		[55]
		>9300	SO-3 ^[1]	7	This work
$1_2 \equiv (\nu_b = 0, \nu_t = 1)$ (3930 cm^{-1})	16800(900)/24900(1900) ^{a,b}				[22]
		36600/42000	SQSBDE ^[24]		[48]
		32300/39000	SQSBDE ^[24]		[50]
		>12500	SO-3 ^[1]	23	This work
$2_1 \equiv (\nu_b = 2, \nu_t = 0)$ (7550 cm^{-1})	160(>80) ^a 50(10) ^a				[35,56]
					[34]
		410(96)	SO-3 ^[1]	64	This work
$2_2 \equiv (\nu_b = 0, \nu_t = 2)$ (7683 cm^{-1})	1730(80) ^a 910(130)-2800(100) ^{a,b} 1090(150)-1800(290) ^{a,b}				[35,56]
					[34]
					[26]
		880(820)	SO-3 ^[1]	64	This work
$2_3 \equiv (\nu_b = 1, \nu_t = 1)$ (7795 cm^{-1})	> 260 330(70) ^a				[35,56]
					[37]
		480(374)	SO-3 ^[1]	60	This work
$3_1 \equiv (\nu_b = 3, \nu_t = 0)$ (11043 cm^{-1})	16				[39]
		280(160)	SO-3 ^[1]	43	This work
$3_2 \equiv (\nu_b = 0, \nu_t = 3)$ (11274 cm^{-1})	1590				[39]
		>1890	SO-3 ^[1]	38	This work

a) Uncertainties are indicated in parentheses as the standard deviation; b) if a range of values is given, this corresponds to different lifetimes for different K-values or different symmetries of sublevels

potential compared with the accurate SO-3 potential indicate that uncertainties arising from the classical approach (compared to quantum) or from the chosen potential (even two already carefully selected ones) are about equally important. Further quantum calculations on the more accurate SO-3 PES should be able to reproduce the mode

specificity in τ_{PD} , observed in experimental investigations in the $N = 1$ and 2 polyads quantitatively. The main drawback of the MD approach is that one finds agreement with experimental data only in a qualitative sense. They nevertheless provide many interesting insights, although quantum effects are definitely very important in $(\text{HF})_2$. The

present results are to be considered as preliminary. To extend our investigations, we plan to enlarge our ensembles by changing the way of providing energy to the dimer in the starting configurations. One can think of using an initial classical state ensemble that mimics the quantum probability distribution of the level considered. We also intend to study excitations involving the low frequency modes. Similar calculations on isotopic dimers are currently in progress in order to compare with our ongoing experiments using cavity ring-down spectroscopy.

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