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Orbiting resonances in the F+HD ($v = 0, 1$) reaction at very low collision energies. A quantum dynamical study

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Abstract

Time-independent, fully converged, quantum dynamical calculations have been performed for the F+HD ($v = 0, j = 0$) and F+HD ($v = 1, j = 0$) reactions on an accurate potential energy surface down to collision energies of 0.01 meV. The two isotopic exit channels, HF+D and DF+H, have been investigated. The calculations reproduce satisfactorily the Feshbach resonance structures for collision energies between 10 and 40 meV, previously reported in the literature for the HF+D channel. Contrary to the results of a former literature work, vibrational excitation of HD is found to enhance reactivity in all cases down to the lowest collision energy investigated. Shape-type orbiting resonances are found for collision energies lower than 2 meV. The resonances appear as peaks in the reaction cross sections that are associated to specific values of the total angular momentum, J . In contrast with the Feshbach resonances at higher energies, the orbiting resonance structure, which is caused by the van der Waals well of the entrance channel, is identical for the HF+D and DF+H exit channels. The orbiting resonance peaks for F+HD ($v = 0$) are very small, but those for F+HD ($v = 1$) could be observed, in principle, with a combination of Raman pumping and merged beams methods.

I Introduction

The F+H₂ system and its isotopic variants have served as a reference for the study of quantum mechanical (QM) resonances in reaction dynamics. In the eighties, the memorable cross-beam experiments of Lee and coworkers [1, 2] disclosed the presence of forward peaks in the vibrationally state-resolved differential cross section (DCS) that were initially attributed to reactive resonances. This was the first claim of a reactive scattering resonance based on experimental data. However, similar forward peaks, albeit less intense, were also obtained in quasiclassical trajectory (QCT) calculations [3] casting doubt on the purely quantum mechanical nature of these peaks. QCT calculations could also account

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satisfactorily for the experimental rate coefficients and isotopic branching ratios [4, 5]. The first reaction resonance unambiguously detected for this system was reported in the work of Skodje *et al.* [6, 7]. A crossed molecular beam experiment on the F+HD isotopic variant of the reaction revealed the presence of a step in the energy evolution of the integral cross section, $\sigma_R(E_{coll})$, for the HF+D output channel at a collision energy of 0.5 kcal/mol (22 meV), which lies below the classical reaction threshold. Accurate quantum mechanical (QM) calculations on the Stark-Werner (SW) potential energy surface (PES) [8] corroborated the resonance character of this feature. Subsequent experimental and theoretical work by X. Yang, D H. Zhang and co-workers led to the discovery of other resonances for the F+H₂ and F+HD isotopic variants of the reaction [9–15]. The sensitive H-atom Rydberg tagging time-of-flight method [16] was used for the search of the resonances, whose presence was mostly revealed by variations in the DCSs or in the products' internal state distributions with collision energy. An alternative procedure based on the photoelectron spectroscopy of the FH₂⁻ and FD₂⁻ anions was employed by Neumark and co-workers [17–20]. The assignment of these new features to reactive resonances was done by comparison to QM dynamical calculations. A recent review of progress in the field of reaction resonances can be found in ref. [21]. The SW PES, used generally hitherto in theoretical studies, could not account for all the new observations and various groups worked on the gradual refinement of the PES using different approaches [22–29]. Detailed discussions on the characteristics and performance of the different surfaces in dynamical calculations can be found in references [30–33]. Specifically the high accuracy of the CSZ PES [29] and of the LWAL PES [26] was stressed in a study by De Fazio *et al.* [33], although, as indicated by Yu *et al.* [34], the CSZ PES accounted better for the photoelectron spectroscopy experiments. A very interesting result obtained by Wang *et al.* [14] is the appearance of dynamical resonances which are only accessible upon vibrational excitation of HD in the F+HD reaction. Similar results were obtained by Yang *et al.* [35] for the Cl+HD reaction. These authors attributed the resonances to bond softening upon vibrational excitation and suggested that this kind of resonances might be common in reactions involving vibrationally excited molecules.

The reaction resonances mentioned thus far are Feshbach-type resonances related with quasi-bound energy levels of the transition state [21, 36]. At very low energies, shape-type orbiting resonances, associated with rotational states trapped behind a centrifugal barrier, can play an important role in many dynamical processes [37, 38]. Orbiting resonances have been experimentally observed in elastic scattering since the seventies [39, 40] and, recently, also in inelastic [41–46] and reactive [47–49] scattering using merged beam techniques which allow the experimental investigation of collisions in the cold ($< 1\text{ K} \sim 1 \times 10^{-4}\text{ eV}$) and near cold regime. The location and width of these resonances provides a sensitive test of the attractive part of the intermolecular potential.

The F+H₂ reaction was also used by Balakrishnan and Dalgarno [50] in their seminal theoretical work on chemical reactivity at ultra-low temperatures. QM calculations carried out by these authors on the SW PES showed that, with decreasing energy, the rate coefficient for the ground state reaction goes through a minimum near 10 K and then reaches a constant value of $1.25 \times 10^{-12}\text{ cm}^3\text{ s}^{-1}$ in the Wigner limit [51] below 0.2 K ($\sim 2 \times 10^{-5}\text{ eV}$), but no

sharp peaks attributable to orbiting resonances were found in the integral reaction cross section for collision energies, E_{coll} , between 10^{-2} and 10^{-7} eV. The low temperature calculations of Balakrishnan and Dalgarno were extended by the same authors to F+HD [52] and by Bodo and Gianturco [53] to F+D₂ and to the $j=2$ and $v=1$ excited states of F+H₂ and F+D₂. In analogy with F+H₂, no orbiting resonance peaks were found for F+D₂ nor for any of the two output channels of F+HD. Rotational excitation of H₂ and D₂ to $j=2$ did not produce great changes in the cross sections, but excitation to $v=1$ led to a pronounced decrease in reactivity for the two isotopic variants. This unexpected result has no clear explanation.

All calculations for F+H₂ and isotopic variants in the cold and ultracold regime mentioned in the previous paragraph were carried out on the SW PES [8] and for the lowest J values (mostly $J=0$, always $J=2$). In a very recent work, published after the submission of this article, De Fazio et al [54] reported a thorough QM study of the dynamics and kinetics of the F+H₂ ($v=0, j=0$) and F+D₂ ($v=0, j=0$) reactions at low and ultralow temperatures. Converged calculations of cross sections and rate constants were presented on the SW PES and on the PES-II of Aquilanti et al. [22, 23] which is derived from the SW PES, but has a different van der Waals well. Shape resonances, specific to each potential surface and isotopic variant, were found in the $E_{coll} \approx 1\text{--}10^{-2}$ meV interval for $J=2$.

In this work we have undertaken a new investigation of the dynamics of this system at very low collision energies on the accurate LWA PES [26]. The calculations, converged in J , were performed for the F+HD ($v=0, 1$) variant, with two distinct output channels which have been often shown to have different dynamical characteristics (see for instance [5, 6, 55–57]). Special emphasis is given to the presence of orbiting resonances, found at very low energies, which are much more pronounced for the reaction with HD ($v=1$). The results are discussed and, where possible, compared to previous work.

II Method

Time independent QM dynamical calculations for the F+HD reaction have been performed using the ABC code of Skouteris *et al.* [58] on the LWA-5 (scaling factor parameter value $s=1.05$) (PES) of Li *et al.* [26].

The scattering matrix in the helicity representation is denoted $S_{v'j'k',vjk}^J$ where v, j, v', j' are the initial and final quantum numbers of the rovibrational states of the reactant and product molecule respectively, k, k' the corresponding helicity quantum numbers and J the total angular momentum quantum number. Values of $S_{v'j'k',vjk}^J$ were obtained for a grid of 22 total energies spanning the 0.236 eV to 0.278 eV energy range for HD ($v=0$), and 22 total energies in the 0.688 to 0.726 eV range for HD ($v=1$). Finer grids of energies were also calculated in order to appreciate the strong, and very narrow, features in the excitation function for both, the $v=0$ and $v=1$, vibrational states of the HD reagent molecule. In this case, 20 total energies were calculated along the 0.23474 to 0.23854 eV interval for the $v=0$ state and 40 additional total energies for the $v=1$ state in the 0.68662 to 0.69325 eV interval. The basis set included all diatomic levels up to a cutoff energy of 3.0 eV and

comprised k quantum numbers until a maximum value of 25. All partial waves till $J_{\max}=18$ were considered and the propagation was extended in 150 sectors up to $18 a_0$. As sometimes stressed in the literature, [28, 59] convergence must be carefully checked when performing calculations for this reaction at low energies. The parameters reported in this article were sufficient to yield cumulative reaction probabilities at $J=0$ converged to better than 0.07% at the lowest total energies.

From the results obtained, reaction probabilities as a function of $J(P_R(J))$, excitation functions (i.e. collision energy dependent integral reaction cross sections, $\sigma_R(E_{coll})$), and differential cross sections, DCS, were derived for the F+HD ($v=0, 1 j=0$) reaction with a methodology entirely similar to that presented in references [58] and [60]. Thus the $P_R(J)$ for a given (v, j) value summed over all v', j', k, k' is given by:

$$P_R(J) = \sum_{j=0}^{J_{\max}} \frac{1}{2\min(J, j)} \sum_{v'j'} \sum_{k, k'} [S_{v'j'k', vjk}^J]^2 \quad (1)$$

The J dependent integral reaction cross sections, $\sigma_R^J(E_{coll})$, can be defined by:

$$\sigma_R^J(E_{coll}) = \frac{\pi}{k^2} \frac{2J+1}{2j+1} \sum_{v'j'} \sum_{k, k'} [S_{v'j'k', vjk}^J]^2 \quad (2)$$

Summing equation 2 over J yields the usual integral cross section:

$$\begin{aligned} \sigma_R(E_{coll}) &= \frac{\pi}{k^2} \sum_{j=0}^{J_{\max}} \frac{2J+1}{2j+1} \sum_{v'j'} \sum_{k, k'} [S_{v'j'k', vjk}^J]^2 = \\ &= \frac{\pi}{k^2} \frac{1}{2j+1} \sum_{j=0}^{J_{\max}} (2J+1) [2\min(J, j) + 1] P_R(J) \end{aligned} \quad (3)$$

In this way

$$\sigma_R(E_{coll}) = \sum_{j=0}^{J_{\max}} \sigma_R^J(E_{coll}) \quad (4)$$

The corresponding DCS can be obtained by the equation:

$$\frac{d\sigma_r(E_{coll})}{d\omega} = \left[\frac{1}{2ik} \sum_J \sum_{v'j'} \sum_{k, k'} (2J+1) d_{k',k}^J(\theta) S_{v'j'k', v, j, k}^J \right]^2 \quad (5)$$

where $d_{k',k}^J(\theta)$ are the rotation matrix elements and θ is the center of mass scattering angle.

III Results and Discussion

Figure 1 displays a comparison of the present calculations with available experimental data showing the presence of reactive resonances for the F+HD reaction. For this comparison, the theoretical results shown are restricted to $E_{coll} > 1.5$ meV. The range of lower collision energies, for which no experimental data have been reported, is considered in detail in the rest of this work. The upper panel represents the excitation function for F+HD ($v=0$) $\rightarrow$ HF+D exit channel. The present calculations are in good agreement with the experimental data of Skodje *et al.* [6, 7] and, specifically, can reproduce the observed resonance feature at 20-30 meV. Quantum dynamical calculations on the SW PES, presented in the same articles, could account for the shape and location of the mentioned feature, although the calculated cross sections between ≈ 20 and 40 meV were larger than the measured ones by a factor of two. The theoretical results showed that the bump in $\sigma_R(E_{coll})$ was due to transition-state resonance at 22 meV localized about a collinear FHD geometry. The resonance was found to be broad with a lifetime of 109 fs, appreciably shorter than the rotational period of the triatomic complex, whose rotational constant was estimated to be $B_0 = 1.8$ cm⁻¹. The resonance state correlates with HF ($v'=3$), but this channel opens at $E_{coll} = 48$ meV and below this energy, the collision complex decays preferentially to HF ($v'=2$), with the reaction proceeding through resonant tunneling. Later work on this resonance [15] improved the agreement between theory and experiment and confirmed the basic picture of its properties. Note that in Figure 1 the theoretical results are somewhat shifted with respect to the experimental measurements. This is most likely due to the fact that the calculations are restricted to HD ($v=0, j=0$) whereas the HD molecular beam contained a population of HD ($v=0, j=1$) close to 20% as discussed, for instance, by De Fazio *et al.* [33]. The lower panel of this figure represents the evolution of the HF backward scattering signal as a function of collision energy for the HF+D channel of the F+HD ($v=0$) and F+HD ($v=1$) reactions. The backward angle (180°) for HF scattering corresponds to the center-of-mass direction of the incoming F atom. In accordance with the experimental observations of Wang *et al.* [14], the calculations predict the occurrence of a maximum at 17.3 meV (0.4 kcal/mol) for the F+HD ($v=0$) reaction, and two maxima at about 9.1 meV (0.21 kcal/mol) and 26.9 meV (0.62 kcal/mol) for the F+HD ($v=1$) reaction that are associated with Feshbach resonances. The relative height of the two calculated maxima for the HD ($v=1$) reaction differs from that observed in the measurements, but taking into account that the evolution of the backward scattering, which considers only a limited fraction of the reactive flux, is a more sensitive test than that of the integral cross section, the agreement is reasonable. The characteristics of these Feshbach resonances are discussed by the authors of ref. [14]. Specifically, the transition state resonances in the F+HD ($v=1$) reaction were found to be trapped in the HD ($v=4$)-F well of the vibrationally adiabatic potential. The good agreement of the calculations with the experimental data corroborates the accuracy of the PES for the investigation of resonances in this reaction.

Figure 2 shows the excitation functions for the two channels of the F+HD ($v=0$) reaction for collision energies from 10^{-2} meV up to 40 meV. The differences in the two channels are

clearly visible. In the DF+H exit channel, the cross section raises monotonically for $E_{coll} > 5$ meV and reaches a value of 0.30 Å^2 for $E_{coll} = 45$ meV. Angular momenta up to $J = 14$ are needed to obtain converged calculations over the whole energy range considered. From a dynamical point of view, this channel is rather "classical" [6, 55] with no specific quantum mechanical features showing off in the excitation function. In contrast, the HF+D exit channel is characterized by the well known non-monotonic broad structure with a maximum at 20 meV due to the Feshbach resonance described above and thoroughly discussed in the literature [6, 7, 15, 30, 33]. With increasing collision energy, an oscillating structure appears which is related with the gradual contribution of higher J values to the broad resonance profile. Toward the low energy end, for $E_{coll} < 5$ meV, there is an increase in the cross sections for the two channels that is discussed below.

Figure 3 represents the excitation functions for the two output channels of F+HD ($v = 1$). The cross section values are larger than those for the reaction with HD ($v = 0$) over the whole energy range considered, and the differences between HF+D and DF+H are still appreciable. The $\sigma_R(E_{coll})$ for the DF+H channel increases monotonically from $E_{coll} > 3$ meV and reaches a value of about 2.5 Å^2 for $E_{coll} = 40$ meV. The cross section for the HF+D channel reaches a maximum of 2.4 Å^2 at about 14 meV, has then a valley at 22 meV followed by a rise, and a plateau of $\sigma_R(E_{coll}) = 2.8 \text{ Å}^2$ until $E_{coll} = 40$ meV. The non monotonic evolution of $\sigma_R(E_{coll})$ over the 5-40 meV range is a smoothed reflection of the resonance structure observed in the backward scattering signal commented on above and displayed in the lower panel of Figure 1. Backward scattering is preferentially caused by a limited fraction of the reactive flux and results in a more neat maxima structure than $\sigma_R(E_{coll})$ which corresponds to integral scattering. A large increase in the cross section, much larger than that mentioned in the preceding paragraph for F+HD ($v = 0$), is also observed in the two channels for collision energies below 5 meV. This region of very low energy is considered in detail in figures 4 and 5. Although the magnitude of the cross sections is certainly different for the HF+D and DF+H pathways, the high similarity in the respective $\sigma_R(E_{coll})$ shapes at these very low collision energies is worth noting. Comparison of figures 4 and 5 to figures 2 and 3 shows that it is in contrast with the cross section behavior at higher energies, which reveals a different dynamics for the two isotopic exit channels as previously described in the literature [6, 55–57].

Figure 4 shows the evolution of $\sigma_R(E_{coll})$ for the F+HD ($v = 0$) reaction at collision energies lower than 4 meV. With decreasing E_{coll} the cross section grows markedly below ≈ 0.5 meV for the two isotopic channels. At $E_{coll} = 0.61$ meV, the $\sigma_R(E_{coll})$ has a small shoulder. It is weak, but it appears in the two channels and is due just to the highest J value ($J = 7$) participating in the reaction at that energy. These two characteristics hint at orbiting resonances. The existence of resonances at very low energies is much more clear for the reaction with vibrationally excited HD. Figure 5 displays $\sigma_R(E_{coll})$ for the two output channels of F+HD ($v = 1$) over the same energy range. Below $E_{coll} = 2$ meV, the excitation functions for the two channels exhibit a characteristic four peak structure due to resonances. The most salient feature in this structure is the very sharp peak at $E_{coll} = 0.41$ meV that reaches a value of 7 Å^2 for DF+H and of 15.4 Å^2 for HF+D. The close similarity between the peak structure of the two channels, leading respectively to DF and HF, excludes the possibility of Feshbach resonances, that would link transition state levels to specific internal

states of the products, and indicates that the peaks are due to entrance channel properties, which are common to the HF+D and DF+H output pathways. On the other hand, the very low collision energies of the observed peaks point to trapping in a van der Waals well at the entrance, resulting in shape-type orbiting resonances. This conclusion is supported by the fact that the peaks are associated with a particular set of J values. Specifically, the very sharp peak just commented on corresponds to $J = 7$. The rest of the peaks are much less intense, but much broader. The isolated peak centered at 1.39 meV is due to $J = 8$. The two lower peaks at $E_{coll} = 0.21$ and 0.36 meV are associated respectively to $J = 3$ and $J = 4$ (not shown for clarity). Note that the E_{coll} values considered in figures 4 and 5 lie below the vibrationally adiabatic barrier for reaction. Under this conditions all the reactivity is due to tunneling.

As mentioned in the introduction, shape-type resonances in the $\approx 1\text{--}10^{-2}$ meV E_{coll} interval were also obtained for the F+H₂ ($v=0, j=0$) and F+D₂ ($v=0, j=0$) reactions in the recent QM calculations of De Fazio et al. [54], performed on the SW and PES II potential surfaces. The resonance peaks were ascribed to specific J values, and their location and magnitude were found to be very sensitive to the topography of the PES in the van der Waals region. Low energy ($E_{coll} \leq 1$ meV) maxima in the reactive cross section were also observed by Lique *et al.* [28] in their QM dynamical calculations for the F_{1/2}+H₂ spin-orbit excited reaction on the LWAL PES. These authors also attributed their findings to shape-type resonances but in that case not to orbiting states at the entrance, but to bound states resulting from trapping behind the centrifugal barrier of the HF ($v' = 3, j' = 3$)+H exit channel.

To illustrate in more detail the characteristics of the orbiting resonances commented on in the previous paragraphs, we consider now reaction probabilities and differential cross sections. Figure 6 displays the reaction probabilities as a function of total angular momentum, $P_R(J)$, for selected collision energies corresponding to peaks in the total reaction cross sections of figures 4 and 5. The two lower panels show results for the vibrational ground state reaction, and the two upper panels for the reaction of HD ($v = 1$). In both cases, the $P_R(J)$ for the HF+D and DF+H exit channels have similar shapes, but different absolute values. In accordance with the magnitude of their respective $\sigma_R(E_{coll})$, the reaction probabilities are smaller for the DF+H channel. In all the cases, the reaction probabilities decrease initially from $J = 0$ and have then maxima for specific J values. The most prominent maxima appear at $J = 7$ for $E_{coll} = 0.41$ meV in the F+HD ($v = 1$) reaction and correspond to the very high peaks in the cross sections of Figure 5. At this collision energy, a secondary maximum, albeit much smaller, is found for $J = 4$. In the rest of cases the maxima are much lower and are always found for the highest J value participating in the reaction at each collision energy, as expected for orbiting. The peak at $J = 8$ for $E_{coll} = 1.39$ meV has also a visible reflection in the corresponding cross section. The $P_R(J)$ for $E_{coll} = 0.21$ and 0.36 meV in F+HD ($v = 1$), peaking at $J = 3$ and $J = 4$ respectively, have not been represented for clarity. Due to the small values of the $P_R(J)$ in F+HD ($v = 0$), the maxima at $E_{coll} = 0.61$ meV translate just into the small shoulders in the $\sigma_R(E_{coll})$ of Figure 4 commented on above. The maxima at $E_{coll} = 1.61$ meV are even lower and the corresponding cross section rise is too small to be appreciable in the scale of Figure 5.

Figure 7 shows differential cross sections for the same collision energies, vibrational states, and isotopic combinations of Figure 6. In all cases, reactive scattering spreads over the whole angular range. The angular distributions are asymmetric, with marked forward and backward peaks at $E_{\text{coll}} = 0.41$ meV for F+HD ($\nu = 1$) and at $E_{\text{coll}} = 0.61$ meV for F+HD ($\nu = 0$). At higher collision energies, $E_{\text{coll}} = 1.61$ meV for F+HD ($\nu = 0$) and $E_{\text{coll}} = 1.39$ meV for F+HD ($\nu = 1$), backward scattering becomes dominant, especially for the HF+D channel. Figure 8 shows the DCSs for $J = 7$ (at the lower collision energies) and $J = 8$ (at the higher collision energies) corresponding to the maxima in the $P_R(J)$ distributions of Figure 6. A complete forward-backward symmetry is now observed in the angular distributions, which is indicative of the formation of a long-lived collision complex lasting for more than a rotational period and losing memory of the original orientation of the reactants before breaking apart [61]. These long-lived complexes are a further resonance evidence. A comparison of figures 7 and 8 shows that for the two exit channels of F+HD ($\nu = 1$), resonance scattering represents a major contribution to the total reactive scattering at $E_{\text{coll}} = 0.41$ meV, and smaller but still appreciable contribution at $E_{\text{coll}} = 1.39$ meV.

In their study of the reactivity of F+H₂ and F+D₂ at very low collision energies with internally hot reagents, Bodo and Gianturco [53] reported that excitation of the H₂ and D₂ molecules to $\nu = 1$ resulted in a pronounced reduction of the reaction cross section for $E_{\text{coll}} < 1$ meV. The authors attributed this unexpected behavior to the loss of an otherwise favorable coupling between the reactants and the products states. It should be noted, however, that the calculations of Bodo and Gianturco were performed on the SW PESs and for J values ≤ 2 . A comparison of figures 2 and 3 of this work shows that there is no decrease in $\sigma_R(E_{\text{coll}})$ upon vibrational excitation for either of the exit channels of F+HD. On the contrary, excitation of HD to $\nu = 1$ leads to a marked increase in reactivity in the cold regime. We have not carried out calculations for the F+H₂ and F+D₂ isotopic variants of the reaction, but one would expect a similar increase in reactivity upon vibrational excitation. Although we have no definitive proof, the present results suggest that the discrepancy with the behavior found by Bodo and Gianturco is due to the fact that their calculations are not converged in J and possibly to the lower accuracy of the SW PES.

The appearance of Feshbach resonances in F+HD ($\nu = 1$) $\rightarrow$ HF+D (see lower panel of Figure 1) has been rationalized by Wang *et al.* [14] as an effect of bond softening induced by vibrational excitation on the adiabatic vibrational well relating reactants and products. The results of this work indicate that vibrational excitation not only affects the HD length modifying the adiabatic well at the transition state, but has also a significant influence on the van der Waals well of the F+HD system that holds orbiting states.

The possible observation of orbiting resonances for the prototype F+HD reaction is certainly most attractive. It poses, without doubt, a formidable experimental challenge, but the development of refined experimental techniques has allowed in recent times, the detection of similar orbiting resonances in inelastic and reactive scattering for other systems [41–49] at collision energies lower than 10^{-2} meV. In these works, the measured resonance structure is often smoothed by the limited experimental resolution, and sometimes displaced from the theoretical predictions, but still observable, specially when a group of resonances appears together (see for instance [43, 49]) as is the case of the present orbiting resonances for F

+HD ($v=1$) at E_{coll} between 0.01 and 0.7 meV. A combination of sophisticated Raman pumping techniques [62], like those used in the experiment of Wang *et al.* [14] for the detection of Feshbach resonances in F+HD ($v=1$), with a merged beams scheme [63] enabling the attainment of very low collision energies could allow, in principle, the investigation of the low energy orbiting resonances predicted in this work.

IV Summary and Conclusions

Fully converged QM calculations of the dynamics of the F+HD ($v=0, j=0$) and F+HD ($v=1, j=0$) reactions have been carried out on an accurate *ab initio* PES for $E_{coll} < 40$ meV, with especial attention to the collision energy interval between 0.01 meV and 4 meV. Experimental features due to Feshbach resonances, previously described in the literature for the HF+D exit channel, are satisfactorily reproduced in the present study. These features are found in the 10-40 meV range and include a maximum in $\sigma_R(E_{coll})$ for the F+HD ($v=0$) reaction [7], and maxima in the evolution of the backward scattering with E_{coll} for F+HD ($v=1$) [14].

The $\sigma_R(E_{coll})$ values for the F+HD ($v=1$) reaction are always appreciably larger than those for F+HD ($v=0$). This result contradicts the prediction of a former work [53] which reported an inhibition in the reactivity of F+H₂ and F+D₂ upon vibrational excitation for $E_{coll} < 1$ meV. The discrepancy is most probably due to the fact that the previous calculations, carried out on a less accurate PES, were not fully converged.

Orbiting resonances are found, for both the F+HD ($v=0$) and F+HD ($v=1$) reactions, at $E_{coll} < 2$ meV. They are manifest as peaks of variable magnitude in the $\sigma_R(E_{coll})$. Unlike the channel-specific Feshbach resonances, which relate transition-state levels with quantum states of the products, these low energy orbiting resonances, associated with levels of a van der Waals well, behind the centrifugal barrier of the entrance channel, have an identical structure for the two isotopic exit channels (HF+D and DF+H) of the reactions. A study of reaction probabilities and differential cross sections further shows that the resonance peaks are associated to the highest J value accessible for a given collision energy, and that for this J , they give rise to long lived collision complexes. The peaks in $\sigma_R(E_{coll})$ for F+HD ($v=0$) are probably too small for experimental detection, but those for F+HD ($v=1$) are comparatively large and might be experimentally observable with a combination of merged beams and Raman pumping techniques.

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Fig. 1.

Top panel: Integral cross section as a function of collision energy, E_{coll} , (excitation function) for the $\text{F}+\text{HD} (\nu=0) \rightarrow \text{HF}+\text{D}$ reaction. Present results: black squares and solid line; experimental results of Skodje *et al.* [7]: blue triangles. Bottom panel: backward scattering signal (180° CM direction) as a function of collision energy for the $\text{F}+\text{HD} (\nu=0, 1) \rightarrow \text{HF}+\text{D}$ reaction. Present results: black solid line and squares stand for HD $\nu=0$ reaction while red solid line and circles represent HD $\nu=1$ reaction; experimental results of Wang *et al.* [14] in blue triangles for both ($\nu=0, 1$) vibrational levels.

Fig. 2.

Excitation function for the $\text{F}+\text{HD} (v=0)$ reaction. Energy calculations span from 0.01 up to 43 meV. Top panel: $\text{HF}+\text{D}$ channel. Bottom panel: $\text{DF}+\text{H}$ channel.

Fig. 3. Excitation function for the $F+HD (v=1)$ reaction. Energy calculations span from 0.01 up to 39 meV. Top panel: $HF+D$ channel. Bottom panel: $DF+H$ channel. Note the vertical axis is broken for clarity.

Fig. 4.

Same as figure 2, but showing the 1-4 meV collision energy interval. In both panels solid circles represent the cross section obtained summed over all partial waves, while the red and light grey lines represent only sums over a specific interval of partial waves. Red line: contributions of total angular momenta from $J=0$ to $J=6$, light grey line: contributions from $J=0$ to $J=7$

Fig. 5.

Same as figure 3, but showing the 1-4 meV collision energy interval. In both panels solid circles stand for the cross section including all partial waves. Dashed red line: cross section obtained by summing partial waves from $J=0$ to $J=6$, blue solid line up to $J=7$, light grey solid line up to $J=8$. Note the vertical axis is broken to show the very sharp peak in the reaction cross section at a collision energy of 0.41 meV.

Fig. 6.

Reaction probability as a function of the total angular momentum for the F+HD ($v = 0, 1$) reaction and both exit channels. Panel (a): F+HD ($v = 1$) $\rightarrow$ HF+D channel; Panel (b): F+HD ($v = 1$) $\rightarrow$ DF+H channel; panel (c): F+HD ($v = 0$) $\rightarrow$ HF+D channel; panel (d): F+HD ($v = 0$) $\rightarrow$ DF+H channel. In panels (a) and (b) the vertical axis is broken for clarity. The collision energies represented correspond to the sharp peaks of the figure 4, panels (c) y (d) and figure 5 for the panels (a) y (c).

Fig. 7. Differential cross section for the F+HD ($\nu = 0, 1$) reaction for the collision energies corresponding to some of the peaks of figure 4 (panels (c) y (d)) and figure 5 (panels (a) and (b)). Panel (a): F+HD ($\nu = 1$) $\rightarrow$ HF + D channel; panel (b): F+HD ($\nu = 1$) $\rightarrow$ DF+H channel; panel (c): F+HD ($\nu = 0$) $\rightarrow$ HF+D channel; panel (d): F+HD ($\nu = 0$) $\rightarrow$ DF+H channel. Note the very different scales for the $\nu = 0$ and $\nu = 1$ reactions.

Fig. 8.

Same as figure 7, but in this case the differential cross section corresponds only to $J = 7$ for 0.41 meV and $J = 8$ for 1.39 meV collision energy. Panels (c) and (d): $J = 7$ for both collision energies. Note the very different scales for the $v=0$ and $v=1$ reactions.