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On the Maximum in the Differential Cross Sections of the $F + H_2$ Reaction in the Region of Small Scattering Angles¹

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Abstract—By means of quantum mechanical simulation of the reaction $F + H_2(v = 0; j = 0, 1, 2) \rightarrow H + HF(v', j')$ on the Stark–Werner ground state potential energy surface at collision energies of 1.84, 2.74, and 3.42 kcal/mol, we have analyzed interference of the “partial waves” corresponding to different values of the total angular momentum J . As the vibrational quantum number v' of the $HF(v', j')$ product increases, the interference for the HF forward scattering becomes noticeably more constructive. This is probably the reason for the maximum in the angular distributions of the $HF(v' = 3)$ molecules at small scattering angles that was discovered experimentally by D.M. Neumark, A.M. Wodtke, G.N. Robinson, C.C. Hayden, and Y.T. Lee, *J. Chem. Phys.* **82** (7), 3045 (1985) at the same collision energies. We have also determined the intervals of J values most effective for forward scattering of the $HF(v', j')$ molecules.

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INTRODUCTION AND STATEMENT OF THE PROBLEM

One of the most explored gas-phase elementary processes involving multi-electron systems is the exothermic exchange reaction $F + H_2 \rightarrow H + HF$ and its isotopomers: $F + D_2$ and $F + HD$ [1, 2]. An extensive bibliography of experimental and theoretical studies of interactions of fluorine atoms with the H_2 , D_2 , and HD molecules is presented in the dissertation [3]. Of the most recent works, one can mention, e.g., the papers [4–6] ($F + H_2$), [7] ($F + D_2$), [8] ($F + HD$), and the reviews [9, 10]. A pioneer role in examining the $F + H_2(D_2, HD)$ reactions was played by the experimental works of Lee's group [11–17]. In particular, the paper [13] reported the vibrationally (but not rotationally) resolved differential cross sections of the HF product scattering from the $F + H_2(v = 0; j = 0, 1, 2)$ reaction obtained in crossed molecular beams at collision energies $E_{col} = 1.84, 2.74$, and 3.42 kcal/mol (79.8, 119, and 148 meV). The paper [14] presented the analogous differential cross sections of the DF product from the $F + D_2(v = 0)$ reaction at $E_{col} = 0.79, 1.82$, and 3.32 kcal/mol (34.3, 78.9, and 144 meV). The most important observation of the works [13, 14] is a maximum in the angular distributions of the HF(DF) products from the $F + H_2(D_2)$ reactions with the highest accessible vibrational quantum number v' , i.e., of $HF(v' = 3)$ and $DF(v' = 4)$, at small scattering angles $\theta \leq 20^\circ$ (in the center-of-mass frame). Here, the value

$\theta = 0$ is defined to correspond to the direction of the F atom motion in the center-of-mass frame. The maximum found in [13, 14] is more pronounced for $F + H_2$ and grows as E_{col} increases for both the reactions. The scattering differential cross sections of the $HF(v' \leq 2)$ and $DF(v' \leq 3)$ molecules do not exhibit such a maximum.

In the works [11–17], the “vibrationally selective” maxima at small θ values in the angular distributions of the $HF(v' = 3)$ and $DF(v' = 4)$ products were regarded as a manifestation of quantum mechanical dynamical (or Feshbach) resonances, i.e., metastable complexes formed in the course of the reaction [18, 19]. However, one then succeeded in reproducing these maxima in quasiclassical trajectory calculations on many potential energy surfaces (PESs) of the $1^2A'$ ground state of the FH_2 system (see the reviews [1, 20, 21] as well as, e.g., the papers [22–26]). This cast doubt on a resonance origin of the maxima. The authors of the work [27] concluded, from an analysis of some quantum mechanical features of the $F + H_2$ interaction, that the maximum in the scattering differential cross sections of the $HF(v' = 3)$ molecules at small θ values is not caused by a resonance. Rather it results from tunneling through the centrifugal barrier (combined with the potential one) at large values of the total angular momentum J . On the other hand, several subsequent studies of the $F + H_2$ reaction (both experimental [28] and theoretical [29–32] ones) presented data in favor of the original resonance explanation of the “vibrationally selective” maximum for $HF(v' = 3)$, see also

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the reviews [9, 18, 19, 33]. On the whole, the question of the nature of the “vibrationally selective” maximum in the angular distributions of the $\text{HF}(\nu' = 3)$ and $\text{DF}(\nu' = 4)$ molecules formed in the $\text{F} + \text{H}_2$ and $\text{F} + \text{D}_2$ reactions remains currently open [5, 10].

In the papers [5, 34], we carried out quantum mechanical calculations of the vibrationally and rotationally resolved differential cross sections $d\sigma_{\nu j'}/d\Omega$ of the HF product scattering from the reaction $\text{F} + \text{H}_2(\nu = 0; j = 0, 1, 2) \rightarrow \text{H} + \text{HF}(\nu', j')$ in the center-of-mass frame for all $0 \leq \nu' \leq 3$ at collision energies $E_{\text{col}} = 1.84, 2.74$, and 3.42 kcal/mol corresponding to the experiment [13] as well as at lower collision energies $E_{\text{col}} = 0.83, 1.27$, and 1.61 kcal/mol (36, 55, and 70 meV) corresponding to the experiment [35]. The calculations were performed on the ab initio Stark–Werner (SW) surface [36], one of the best PESs of the $1^2A'$ ground state of the FH_2 system [1–3, 20, 21, 23–27, 37], by means of the ABC program described in detail in the work [38]. In this program, the Schrödinger equation for the motion of three nuclei on the PES in question is solved by the coupled-channel method in the Delves hyperspherical coordinates, see [39]. The quantum scattering boundary conditions in the ABC program are applied exactly (without the use of complex absorbing potentials), and for each value of the total angular momentum J , the coupling between the initial $(\mathbf{l}, j)$ and final $(\mathbf{l}', j')$ orbital and rotational angular momenta is also taken into account without any approximations. Quantum mechanical simulation of the $\text{F} + \text{H}_2(\text{D}_2, \text{HD})$ reactions on the SW surface by means of the ABC code or other similar programs enables one to reproduce a good many experimental data on the dynamics of these reactions, including the maximum at small θ values in the angular distributions of the $\text{HF}(\nu' = 3)$ and $\text{DF}(\nu' = 4)$ products from chemical scattering of F on H_2 and D_2 , respectively [1–3, 21, 24, 26, 27, 37].

As was shown in the work [5], the “vibrationally selective” maximum (discovered in the experiment [13]) in the angular distribution of the $\text{HF}(\nu' = 3)$ products from the $\text{F} + \text{H}_2$ reaction in the region of small θ angles ($0^\circ \leq \theta \leq 20^\circ$) is caused by the different behaviors of the differential cross sections of the HF scattering not only with respect to the vibrational quantum number ν' but also with respect to the rotational quantum number j' . This maximum is “rotationally cold” [5]: the main contribution to it is made by the $\text{HF}(\nu' = 3; j')$ products with $j' \leq 3$ or, in the case of the $\text{F} + \text{H}_2(\nu = 0; j = 2)$ reaction, with $j' \leq 4$ (which agrees with the data of the papers [22, 24]). Moreover, the maximum results from a superposition of two effects which are independent but reinforce each other. First, the maxima in the rotationally resolved differential cross sections $d\sigma_{\nu j'}/d\Omega$ in the region of small scattering angles θ are present for small j' numbers only ($j' \leq 4$ or $j' \leq 5$). At the same time, for $\nu' \leq 2$, the $\text{HF}(\nu', j')$ products with small j' numbers consti-

tute a not so large fraction of all the $\text{HF}(\nu')$ molecules in the given vibrational state ν' but for $\nu' = 3$, all the appearing $\text{HF}(\nu' = 3; j')$ products are characterized by small rotational quantum numbers j' due to energy restrictions. It is worthwhile to emphasize that this effect is not related to any resonances. Second, the larger ν' is, the more pronounced are the maxima themselves in the cross sections $d\sigma_{\nu j'}/d\Omega$ at small θ values for small j' numbers. This trend affects all the four vibrational states ν' of the HF product and is hardly of a mainly resonance origin as well. Thus, the results of the work [5] are a new evidence against a substantial role of resonances in the formation of a maximum in the angular distribution of the $\text{HF}(\nu' = 3)$ molecules in the region of small scattering angles. Note that the maximum at small θ values in the scattering differential cross sections of the $\text{DF}(\nu' = 4)$ products from the $\text{F} + \text{D}_2$ reaction is also “rotationally cold” [25, 26].

The authors of the papers [24, 27] analyzed the contributions, to the total and differential cross sections of the $\text{F} + \text{H}_2$ scattering, from the “partial waves” corresponding to various values of the total angular momentum J . Of course, because of interference effects, one cannot speak of “contributions” in this context in the strict sense. In the work [27], this investigation was carried out by quantum mechanically simulating the $\text{F} + \text{H}_2(\nu = 0; j = 0, 1)$ reaction at the energies of the experiment [13] on the SW surface. In the work [24], quasiclassical and quantum mechanical calculations for the $\text{F} + \text{H}_2(\nu = j = 0)$ reaction were performed at collision energy $E_{\text{col}} = 3.69$ kcal/mol = 160 meV on two PESs, namely, SW and Hartke–Stark–Werner (HSW) [40]. The analysis of [24, 27] pertained to rotationally unresolved scattering $\text{F} + \text{H}_2(\nu = 0; j) \rightarrow \text{H} + \text{HF}(\nu')$. In the present note which is a continuation of the works [5, 34], we consider the contributions from various “partial waves” to the rotationally resolved scattering differential cross sections $d\sigma_{\nu j'}/d\Omega$ of the reaction $\text{F} + \text{H}_2(\nu = 0; j = 0, 1, 2) \rightarrow \text{H} + \text{HF}(\nu', j')$ in the region of small θ angles at the energies of the experiment [13]. A study of the “partial wave” interference allows one to get supplementary information on the origin of the maximum in the angular distribution of the $\text{HF}(\nu' = 3)$ products. Notice that an analysis of the “partial wave” interaction is feasible only in the framework of quantum mechanical simulation of the process. No experimental data are available here, and it seems to be impossible at present to raise any suitable experiment.

DESCRIPTION OF THE RESULTS

Just as in our preceding paper [5], quantum mechanical simulation of the $\text{F} + \text{H}_2(\nu = 0; j)$ reaction was carried out for $j = 0, 1$, and 2 at each collision energy $E_{\text{col}} = 1.84, 2.74$, and 3.42 kcal/mol on the SW surface [36] of the $1^2A'$ ground state of the FH_2 system

by means of the ABC program [38]. The calculations were performed for the total angular momentum J from 0 to its maximal value $J_{\max}$ equal to 25 for $E_{\text{col}} = 1.84$ kcal/mol and equal to 30 for the two higher collision energies. We used the same values of the convergence parameters of the ABC program as in the work [5].

The $1^2A'$ state of the FH_2 system correlates with the ground states of the reagents $\text{F}(^2P_{3/2}) + \text{H}_2(^1\Sigma_g^+)$ and the products $\text{H}(^2S_{1/2}) + \text{HF}(^1\Sigma^+)$. Besides the $1^2A'$ ground state, two more electronic states of the FH_2 system are essential at collision energies no higher than ≈ 1 eV (23.06 kcal/mol), namely, the $2^2A''$ state which also correlates with the $^2P_{3/2}$ ground state of the fluorine atom and the $2^2A'$ state which correlates with the excited state $\text{F}^*(^2P_{1/2})$ [1, 3, 6, 41–44]. However, both the excited states $2^2A''$ and $2^2A'$ of the FH_2 system correlate with excited states of the HF molecule (namely, $^3\Pi_2$ and $^3\Pi_1$), and the corresponding PESs are therefore strongly endothermic [1, 3, 6, 41–44]. Consequently, the $2^2A''$ state of the FH_2 system does not participate in the reaction $\text{F} + \text{H}_2 \rightarrow \text{H} + \text{HF}$ (it is of importance to take this state into account only while simulating elastic and inelastic scattering [45]), and the $2^2A'$ state (which is of the same symmetry as the ground state) can contribute to the reaction only via the nonadiabatic transition $2^2A' \rightarrow 1^2A'$ [1, 3, 6, 41–44]. As the calculated data of the works [6, 44] show (see also the review [46]), the ratio of the reactivities of the excited ($^2P_{1/2}$) and ground ($^2P_{3/2}$) states of a fluorine atom in interactions with H_2 decreases rapidly as the collision energy increases. At the energies considered in the present paper ($E_{\text{col}} \geq 1.84$ kcal/mol), the contribution from $\text{F}(^2P_{3/2})$ completely dominates for all the vibrational quantum numbers v' of the HF molecule. Moreover, the results of the work [37] imply that at $E_{\text{col}} = 81$ meV (1.87 kcal/mol), the non-adiabatic transitions $2^2A' \rightarrow 1^2A'$ do not affect scattering of the $\text{HF}(v' = 1)$ and $\text{HF}(v' = 2)$ products from the $\text{F} + \text{H}_2(v = 0; j = 0, 1)$ reaction almost at all. Thus, neglecting the contribution from the excited state $2^2A'$ of the FH_2 system to the reaction dynamics should be regarded as entirely justified in the context of the present paper (as well as of the preceding work [5]). Simulation of the process on a single surface of the $1^2A'$ ground state is sufficient for reproducing the maximum at small θ values in the angular distributions of the $\text{HF}(v' = 3)$ and $\text{DF}(v' = 4)$ products from the $\text{F} + \text{H}_2$ and $\text{F} + \text{D}_2$ reactions, respectively [1–3, 21, 24, 26, 27].

Denote by $X_{v'j'}^J(\theta)$ the differential cross section of the $\text{HF}(v', j')$ product scattering obtained by taking

into account the total angular momenta from 0 to a given J for E_{col} and j fixed [5, 27, 32, 34, 38, 47]:

$$X_{v'j'}^J(\theta) = \frac{\hbar^2}{8\mu E_{\text{col}}(2j+1)} \sum_{k'=-j'}^{j'} \sum_{k=-j}^j |F_{v'j'kk}^J(\theta)|^2,$$

where

$$F_{v'j'kk}^J(\theta) = \sum_{I=\max(|k'|, |k|)}^J (2I+1) d_{k'k}^I(\pi-\theta) S_{v'j'k', 0jk}^I(E_{\text{col}}).$$

Here, μ is the reduced mass of the F and H_2 reagents, k is the helicity quantum number of the H_2 molecule (the projection of the angular momentum of H_2 onto the direction of the relative velocity of the reagents), k' is the helicity quantum number of the HF molecule (the projection of the angular momentum of HF onto the direction of the relative velocity of the products), $d_{k'k}^I$ are the reduced elements of the Wigner rotation matrix [48, 49], and $S_{v'j'k', 0jk}^I(E_{\text{col}})$ denote the complex elements of the S -matrix in the helicity representation [38, 47]. The presence of excited states of the FH_2 system gives rise to an additional factor even if these states are not involved in the reaction (see discussion in [41–43]). However, we neglect this factor because it is completely inessential for a comparative analysis of the role of various J values and the accompanying interference effects. The use of $\pi-\theta$ in place of θ as the argument of the $d_{k'k}^I$ functions is related to the direction of counting the θ angle accepted in studies of the $\text{F} + \text{H}_2(\text{D}_2, \text{HD})$ reactions (see discussion in the paper [27]). For $J < |k|$ or $J < |k'|$, the $F_{v'j'kk}^J(\theta)$ function vanishes identically. It is clear that $X_{v'j'}^\infty = d\sigma_{v'j'}/d\Omega$.

It is natural to regard the difference $X_{v'j'}^J(\theta) - X_{v'j'}^{J-1}(\theta)$ as the contribution to the cross section $d\sigma_{v'j'}/d\Omega$ from the “partial wave” corresponding to the given J value (for $J = 0$, we set $X_{v'j'}^{-1}(\theta)$ to be identically equal to zero). Due to interference effects, this contribution can be negative for some θ angles. The same approach to “partial wave” analysis was employed in the work [27]. Note that the maximum in the angular distribution of the $\text{HF}(v' = 3)$ molecules at small θ values is located within the interval $0^\circ \leq \theta \leq 20^\circ$ in almost all the cases [5, 13]. Consequently, we measured the contribution from the “partial wave” corresponding to the given J value to forward scattering of the $\text{HF}(v', j')$ products by the integral

$$Y_{v'j'}^J = \int_{0^\circ}^{20^\circ} [X_{v'j'}^J(\theta) - X_{v'j'}^{J-1}(\theta)] d\theta. \quad (1)$$

Fig. 1. The fraction of the “partial waves” with negative contributions to forward scattering of the HF(v' , j') products from the F + H₂($v = 0$; j) reaction at various collision energy values $E_{\text{col}} = 1.84$ (circles), 2.74 (squares), and 3.42 kcal/mol (triangles). The solid lines correspond to the value $j = 0$ of the initial rotational quantum number of the H₂ reagent, the dashed lines, to the value $j = 1$, and the dotted lines, to the value $j = 2$.

Such integrals were calculated by the Gregory quadrature formula (20.7–15.0) from the handbook [50] with a step of 0.5° .

For any values of E_{col} , j , v' , and j' , we determined the fraction $z_{v,j'}$ of negative $Y_{v,j'}^J$ quantities (among all the nonzero numbers $Y_{v,j'}^0$, $Y_{v,j'}^1$, ...). The results are presented in Fig. 1. A small fraction of negative $Y_{v,j'}^J$ integrals means mainly *constructive* interference of the “partial waves” in the HF(v' , j') product scattering at small θ angles (almost every “partial wave” in the region $\theta \leq 20^\circ$ *strengthens* the sum of the waves corresponding to the smaller J momenta), whereas a large fraction indicates mainly *destructive* interference (many of the “partial waves” in the region $\theta \leq 20^\circ$ *reduce* the sums of the waves corresponding to the previous values of the total angular momentum J). As is seen in Fig. 1, the $z_{v,j'}$ quantity exhibits a trend to decrease as the initial rotational quantum number j of the H₂ reagent increases and also as the vibrational quantum number v' of the HF product grows. In the

first case, this tendency is not well pronounced whereas in the second case, it is very clear (especially as one passes from $v' = 2$ to 3). The fraction of negative $Y_{v,j'}^J$ integrals lies between 20% and 60% for the overwhelming majority of the values of E_{col} , j , and j' for $v' = 0$, between 20% and 50% for $v' = 1$, and between 10% and 45% for $v' = 2$. Finally, for $v' = 3$, this fraction does not exceed 35% in all the cases and is no greater than 25% for $j' \leq 4$. Moreover, for many of the sets (E_{col} , j , j') for $v' = 3$, all the $Y_{3,j'}^J$ integrals are non-negative (and the fraction $z_{3,j'}$ attains a minimum at $j' = 1$ or 2 for E_{col} and j fixed). The total fraction of negative $Y_{v,j'}^J$ quantities over all the values of E_{col} , j , j' , and J equals to 40.4%, 36.7%, 27.1%, and 7.2% for $v' = 0$, 1, 2, and 3, respectively. We think that this increase in constructive character of the “partial wave” interference for the HF(v') forward scattering as v' grows is the main reason (or one of the main reasons) why for small j' numbers, the larger v' is, the more pronounced are the maxima in the differential

Fig. 2. The mean value of the total angular momentum J calculated with taking into account the contributions from various “partial waves” to forward scattering of the $\text{HF}(v', j')$ products from the $\text{F} + \text{H}_2(v=0; j)$ reaction. The notation is the same as in Fig. 1.

cross sections $d\sigma_{vj'}/d\Omega$ in the region of small scattering angles θ .

Note that the total fractions of negative $Y_{vj'}^J$ quantities over all the values of j, j' , and J are equal to (44.1, 39.9, 38.4), (40.7, 36.5, 34.0), (30.9, 27.6, 23.8), and (5.0, 7.7, 7.9) for $v' = 0, 1, 2$, and 3, respectively, where each pair of parentheses contains the fractions for $E_{\text{col}} = 1.84, 2.74$, and 3.42 kcal/mol (per cent). For any fixed value of v' , these fractions decrease as E_{col} grows (except for the case $v' = 3$ where the opposite trend holds). On the other hand, the total fractions of negative $Y_{vj'}^J$ quantities over all the values of E_{col}, j' , and J are equal to (46.5, 40.5, 34.5), (40.0, 37.2, 33.1), (31.6, 26.7, 23.3), and (13.7, 6.9, 3.0) for $v' = 0, 1, 2$, and 3, respectively, where each pair of parentheses lists the fractions for $j = 0, 1$, and 2 (per cent). For any fixed value of v' , these fractions decrease as j increases.

An almost constructive character of the “partial wave” interference for forward scattering of the $\text{HF}(v' = 3)$ molecules was pointed out in the paper [27]. However, the analysis of [27] was confined to the rotationally unresolved angular distributions and was

not carried over to the values $v' \leq 2$ of the vibrational quantum number of the HF product.

We considered it justifiable that the mean value $\langle J \rangle$ of the J numbers taken with the weights $\max(Y_{vj'}^J, 0) = (1/2)(|Y_{vj'}^J| + Y_{vj'}^J)$,

$$\langle J \rangle = \left[\sum_{J=0}^{J_{\text{max}}} \max(Y_{vj'}^J, 0) \right]^{-1} \sum_{J=0}^{J_{\text{max}}} J \max(Y_{vj'}^J, 0), \quad (2)$$

indicates the total angular momenta J most effective for scattering of the $\text{HF}(v', j')$ molecules at small θ angles (or in any case some range of such angular momenta). The values $\langle J \rangle$ for all E_{col}, j, v' , and j' are presented in Fig. 2.

As is seen in Fig. 2, the quantities $\langle J \rangle$ increase on the whole as E_{col} and j grow which agrees with the results of the work [27]. The dependence of $\langle J \rangle$ on j' is far more complicated. For $v' = 0$ and 1, the numbers $\langle J \rangle$ for $j = 0$ increase rapidly as j' is enhanced starting with $j' \approx 10$ (for all the three collision energies). For $j = 1$ and 2, such an increase in the case $v' = 0$ is observed in the range $9 \leq j' \leq 14$ for $E_{\text{col}} = 2.74$ and

3.42 kcal/mol only. In the case $v' = 1$, on the other hand, the dependence of $\langle J \rangle$ on j' for $j = 1$ or 2 fixed is characterized first of all by a minimum at $j' = 11$ or 12 (for all the three collision energies). For $v' = 2$ and 3 , the dependence of the quantity $\langle J \rangle$ on j' is much weaker than for $v' = 0$ and 1 .

For small $j' \leq 5$ (recall that the maximum in the cross sections $d\sigma_{vj'}/d\Omega$ in the region of small scattering angles θ is present for such values of j' only), the numbers $\langle J \rangle$ lie between 3 and 10 for all the values of E_{col} and j for $v' = 0$, between 8.0 and 15.2 for $v' = 1$, between 11.0 and 19.3 for $v' = 2$, and between 10.5 and 20.0 for $v' = 3$. For $v' \geq 2$, the quantities $\langle J \rangle$ lie near the lower bound of the classically forbidden range of the values of the total angular momentum [23, 27]. For $v' \leq 1$, the numbers $\langle J \rangle$ for $j' \leq 5$ depend on j more than on E_{col} . For $v' = 3$, on the other hand, the main parameter of the $F + H_2$ interaction to determine $\langle J \rangle$ for small j' values is the collision energy E_{col} rather than the initial rotational quantum number j of the H_2 reagent.

The fact that the curves of the dependence of $\langle J \rangle$ on $j' \leq 5$ for fixed values of E_{col} and j change rather slightly as one passes from $v' = 2$ to 3 (Fig. 2) is an additional evidence against a mainly resonance nature of the maximum in the angular distribution of the $HF(v' = 3)$ molecules in the region of small scattering angles.

Note that a priori one may propose another (and more "direct") way to calculate the contribution to the cross section $d\sigma_{vj'}/d\Omega$ from the "partial wave" corresponding to a given value of the total angular momentum J . This way consists in taking into account only this value of J while computing the cross section. Otherwise speaking, one may propose to consider the quantities

$$\Xi_{vj'}^J(\theta) = \frac{\hbar^2}{8\mu E_{\text{col}}(2j+1)} \sum_{k'=-j'}^j \sum_{k=-j}^j |\Phi_{vj'k'k}^J(\theta)|^2$$

instead of the differences $X_{vj'}^J(\theta) - X_{vj'}^{J-1}(\theta)$, where

$$\Phi_{vj'k'k}^J(\theta) = (2J+1)d_{k'k}^J(\pi-\theta)S_{vj'k',0jk}^J(E_{\text{col}})$$

(for $J < |k|$ or $J < |k'|$, the $\Phi_{vj'k'k}^J(\theta)$ function vanishes identically), and to consider the integrals

$$\Psi_{vj'}^J = \int_{0^\circ}^{20^\circ} \Xi_{vj'}^J(\theta) d\theta$$

instead of the integrals (1). However, such an approach does not enable one to estimate the "partial wave" interference. Moreover, we have verified that for $v' \geq 1$, the numbers

$$\left(\sum_{J=0}^{J_{\text{max}}} \Psi_{vj'}^J \right)^{-1} \sum_{J=0}^{J_{\text{max}}} J \Psi_{vj'}^J$$

turn out to be much smaller than the quantities $\langle J \rangle$ found by formula (2) (the larger v' is, the stronger is the understating).

We think that it would be interesting to carry out a similar "partial wave" analysis of the $F + H_2$ reaction on other PESs of the FH_2 system (for instance, on the surfaces employed in the recent papers [4, 6, 8]) as well as that of the $F + D_2$ reaction at the energies of the experiment [14].

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