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ARTICLES

Reduced Dimensionality Quantum Scattering Calculations on the $F + CH_4 \rightarrow FH + CH_3$ Reaction

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The existence of recently observed scattering resonances in the hydrogen abstraction reaction $F + CH_4 \rightarrow FH + CH_3$ was investigated using the reduced dimensionality rotating line umbrella (RLU) quantum scattering model and employing an analytical potential energy surface, PES-2006, recently developed by our group. The calculations were performed in hyperspherical coordinates. The wells found in the hyperspherical adiabats, the oscillatory pattern in the cumulative and state-to-state reaction probabilities, the forward/backward predominance in the differential cross section at a collision energy of 1.8 kcal mol^{-1}, and the dramatic change of the scattering angle with energy are related to scattering resonances, and they are assigned to a quasi-bound complex on the vibrationally adiabatic ground-state potential.

1. Introduction

The polyatomic $F(^2P) + CH_4 \rightarrow FH(\nu') + CH_3$ reaction presents several important features that invite both theoretical and experimental investigations. The reaction path is difficult to calculate because the potential energy surface is very flat in the entrance channel. The kinetics and dynamics data are of particular interest because of the $FH(\nu')$ vibrational population inversion produced in this reaction, which constitutes a chemical laser system. Moreover, recently Shiu et al.[1] experimentally reported the existence of reactive resonances, Feshbach-type, for this reaction, using a rotating-source crossed-beam apparatus. Further, three theoretical papers[2−4] appeared to explain this observation using different potential energy surfaces. The first paper[2] associates the shape of the potential with the formation of reaction scattering resonance states, while the last papers[3−4] analyzed reaction probabilities and integral cross sections using quantum dynamics calculations with the semirigid vibrating rotor target (SVRT) method.

Our group has given much attention to this reaction in recent years. In 1996, we reported[5] for the first time an analytical potential energy surface (PES) for the title reaction (PES-1996), which was modified and updated in 2005[6] to correct its most obvious deficiencies. This last surface was symmetric with respect to any permutation of the four methane hydrogen atoms, and it was calibrated to reproduce the experimental rate constants. To analyze the effect of the spin−orbit electronic states of the fluorine atom, $^2P_{3/2}$ and $^2P_{1/2}$, two versions were constructed, called PES-SO and PES-NOSO, the latter also being named PES-2005. Both PES-1996 and PES-2005 were calibrated from kinetics aspects, such as forward rate constants and kinetic isotope effects (KIEs). Shortly after we had constructed PES-2005, two dynamics studies using quasi-classical trajectory (QCT) calculations[7,8] questioned the suitability of this analytical surface to describe the dynamics of this reaction, and they reported four major drawbacks in PES-

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2005. First, the energy drop along the reaction path in the product valley does not reproduce ab initio calculations. Second, the surface neglects the FH...CH_3 van der Waals minimum in this product valley. Third, PES-2005 shows much less FH(ν') vibrational excitation than seen in experiments. And fourth, the FH(ν') rotational distribution is considerably hotter than experiment. To correct the deficiencies of PES-2005, we recently[9] constructed a new analytical potential energy surface for the title reaction, named PES-2006.

The main differences between PES-2006 and the earlier surfaces[5,6] result from the calibration process. The criteria chosen for PES-2006 were broader than in previous works of our group.[5,6] The main innovation with respect to the earlier surfaces is that we tried to reproduce the topology of the reaction, from reactants to products, with special care taken in the reproduction of ab initio information along the reaction path and the investigation of complexes in the entrance and exit channels. Therefore, for PES-2006 we did not limit the calibration to the zone close to the saddle point.[9] On this surface, we studied exhaustively the kinetics, using variational transition-state theory (VTST) with semi-classical transmission coefficients, as well as the dynamics using quasi-classical trajectory (QCT) calculations including corrections related to zero-point energy leakage along the trajectories. We concluded that the reasonable agreement with experiment (always qualitative and sometimes quantitative) lends confidence to PES-2006.

Using PES-2006 in quasi-classical trajectory (QCT) calculations[9] we found an oscillatory pattern in the excitation function, forward/backward predominance in the differential cross-section analysis at 1.8 kcal mol^{-1}, and dramatic changes in the differential cross section−collision energy−scattering angle (DCS-Ec-θ) 3D representation, which are signatures of the resonance reported experimentally by Shiu et al.[1] and which were assigned to wells in the vibrationally adiabatic curves found in our surface. Obviously, the classical nature of the QCT calculations means that this conclusion was only tentative, and quantum-mechanical (QM) calculations will be required for a firmer conclusion to be drawn.

To go deeper into the understanding of the title reaction and the role of the reactive resonance, in the present paper we perform reduced dimensionality quantum scattering (QM) calculations on PES-2006 and compare the results with experimental information and previous QCT results[9] on the same surface. The article is structured as follows. In section 2 we present the computational procedure in the reduced dimensionality QM scattering calculation, and in section 3 we briefly outline the potential energy surface. The QM dynamics results are presented and compared with QCT calculations and experimental values in section 4. Finally, section 5 contains the conclusions.

2. Quantum Dynamics and Formulation

Despite the progress in the field of quantum dynamics, it is still not possible to obtain integral or differential cross sections from a full-dimensional quantum dynamics calculation for a reaction involving six atoms. For this reason we treat the present six-atom reaction using reduced dimensionality quantum scattering calculations. We employ the rotating line umbrella (RLU) model, which was previously developed and extensively described by Yu and Nyman.[10−12] In this model, three degrees of freedom are treated explicitly quantum dynamically. For the F + CH_4 → FH + CH_3 reaction, the forming F−H stretch vibration, the breaking C−H stretch vibration, and the umbrella-type motion are treated explicitly.

The effect of the zero-point energies of the degrees of freedom not treated in the RLU model is dealt with by approximately including that zero-point energy in the potential energy surface. Here this was done similar to our previous treatment for the Cl + CH_4 reaction, that is, we set

$$V_{\mathrm{eff}}(R) = V(R) + \Delta V_{\mathrm{corr}}$$

$$\Delta V_{\mathrm{corr}} = \frac{1}{2} V_{\mathrm{c}}\{1 - \tanh[\eta(R - R_{\eta})]\}$$

where $V(R)$ is the ordinary potential energy surface, that is, PES-2006, and ΔV_{corr} is the zero-point energy correction. R is the C−H bond distance of the breaking bond and the parameters are $V_c = 0.18647$ eV, $\eta = 5.0$ bohr^{-1}, and $R_\eta = 2.8$ bohr.

As the time-independent implementation of the RLU model has been described previously,[10−12] we only give values of those parameters which are varied in order to achieve converged results under different conditions or for different reactions. Using the symbols and terminology of ref 12, the hyperradius was propagated from 4.0 to 25.0 bohr using about 700 sectors and an adiabatic basis of 80 functions. The potential cutoff was set to 4.5 eV. The z-range was set to [−1.9, 1.9] bohr and treated with 60 Fourier DVRs. 120 DVRs were used for the hyperangle φ. The C−H bond length of the unreactive bonds was held fixed at 2.06736 bohr.

3. Potential Energy Surface

Recently our group constructed a new PES for the gas-phase F + CH_4 → FH + CH_3 polyatomic reaction,[9] PES-2006, which is symmetric with respect to the permutation of the methane hydrogen atoms, a feature especially interesting for dynamics calculations. The functional form was developed in that work, and therefore will not be repeated here. Basically, the PES consists of four London-Eyring-Polanyi (LEP) stretching terms, augmented by out-of-plane bending and valence bending terms. In the calibration process, we fitted some of the parameters of the analytical PES to reproduce the variation of the experimental thermal forward rate constants with temperature (as in earlier papers of our group) and the topology of the reaction from reactants to product with special care taken in the reproduction of ab initio information along the reaction path and the investigation of complexes in the entry and exit channels, which was an innovation with respect to earlier papers.[5,6] In this very exothermic reaction, $\Delta H_r(0\ \mathrm{K}) = -32.0$ kcal mol^{-1}, with a very low barrier height, $\Delta E^{\ddagger} = 0.35$ kcal mol^{-1} ($\Delta H^{\ddagger}(0\ \mathrm{K}) = -0.07$ kcal mol^{-1}), we found on the ground-state vibrationally adiabatic curve, ΔV_a^G, a potential well stabilized by 3.03 kcal mol^{-1} with respect to the products, in the exit channel, with the following geometry: F−H′ = 2.217 bohr, and C−H′ = 2.611 bohr. Two important features were noted in that paper.[9] First, this well does not correspond to the van der Waals complex found closer to the products, with the following geometry: F−H′ = 1.735 bohr and C−H′ = 3.779 bohr; and second, the mechanism that assumes the presence of a quasi-bound complex does not exclude the possibility of a direct mechanism, rather both mechanisms take place simultaneously.

Because of the abundant experimental information available for this reaction, PES-2006 was subjected to a great variety of tests, of both kinetic and dynamic types. Thus, from the kinetics point of view, first, the forward thermal rate constants calculated using variational transition-state theory (VTST) with semi-classical transmission coefficients agreed with experimental measurements, reproducing the Arrhenius plot. Second, we found good agreement at several temperatures of the CH_4/CD_4

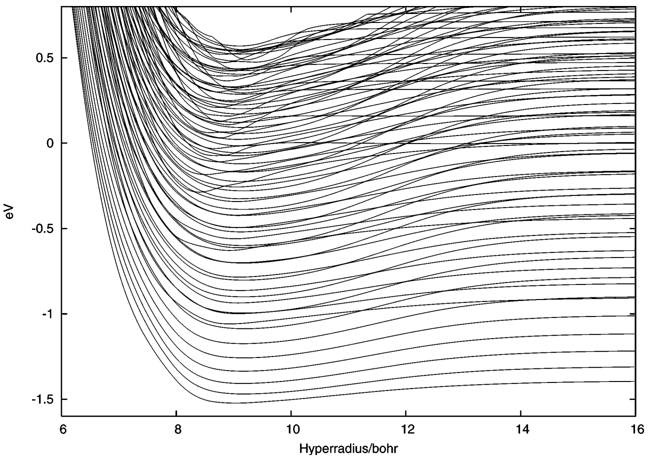

Figure 1. Hyperspherical adiabatic energy levels for the F + CH_4 reaction as a function of hyperradius ρ (bohr). The energies (eV) are relative to the bottom of the asymptotic F + CH_4 potential.

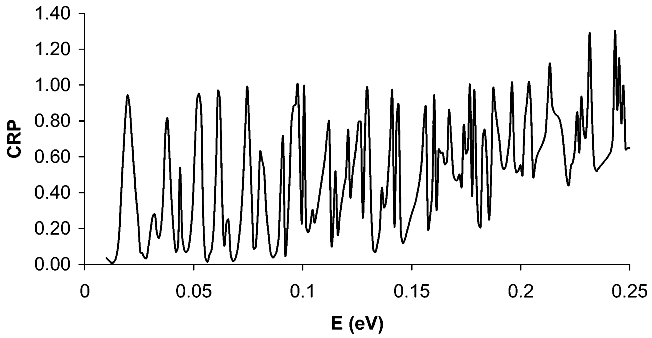

Figure 2. Cumulative reaction probabilities versus total energy for the F + CH_4 reaction.

kinetic isotope effects (KIEs). The rates and the KIEs are sensitive tests of features of the new surface, such as barrier height and width, zero-point energy, and the tunneling effect. From the dynamics point of view, an extensive study employing quasi-classical trajectory (QCT) calculations was performed on this surface. First, we found that the FH(ν',j') rovibrational distributions agree with experiment. Second, the state-specific scattering distributions present qualitative agreement with experiment, and as the FH(ν') vibrational state increases, the scattering angle becomes more forward. Third, the oscillatory pattern in the excitation function, the forward/backward predominance in the differential cross section (DCS) analysis at 1.8 kcal mol^{-1}, and the dramatic change in the three-dimensional "DCS−collision energy−scattering angle" plot are signatures of the resonance reported experimentally by Shiu et al.,[1] and assigned to quasi-bound states in the vibrationally adiabatic curve as found for our surface. Obviously, the classical nature of the QCT calculations means that this conclusion is only tentative, and quantum-mechanical (QM) calculations will be required for a firmer conclusion to be drawn.

An additional test of PES-2006 was performed by analyzing the kinetics and dynamics of the isotope analogue F + $CD_4 \rightarrow$ FD + CD_3 reaction,[13] using also QCT calculations for collision energies in the range 0.3−6.0 kcal mol^{-1}. While the CD_3 coproduct appears vibrationally and rotationally cold, in agreement with experiment, most of the available energy appears as FD(ν') product vibrational energy, peaking at $\nu' = 3$, one vibrational level lower than found experimentally. The excitation function reproduces the experiment, with the maximum contribution from the most populated FD($\nu' = 3$) level. The state-specific scattering distributions at different collision energies also reproduce the experimental behavior, with a clear propensity toward forward scattering. This tendency increases with the energy.

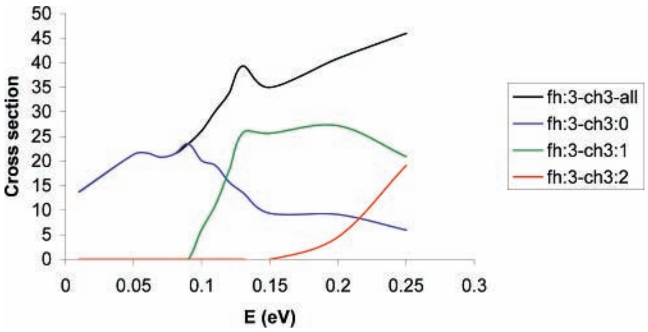

Figure 3. Reaction cross sections (arbitrary units) for reaction of ground-state F + CH_4 forming products in the FH(v′ = 3) + CH_3(v′ = 0,1,2) states.

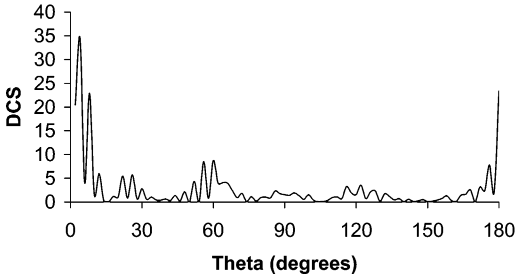

Figure 4. State-to-state differential cross sections for ground-state reactants at a collision energy of 1.8 kcal mol^{-1} forming FH(v′ = 3) + CH_3(v′ = 0).

Finally, the comparison of the dynamics results for the title reaction, F + CH_4, with those for the analogous F + CD_4 reaction showed different behavior of the excitation function and of the evolution of the differential cross section with collision energy. These different patterns seem to indicate that the two reactions follow different mechanisms. In summary, the reasonable agreement with the abundant experimental information lends confidence to PES-2006, although there are some differences, which may be due to the PES itself, but also to the known limitations of the QCT method (especially the treatment of the vibrational ZPE, i.e., the ZPE breakdown problem).

4. Results and Discussion

4.1. Hyperspherical Adiabats. Figure 1 shows hyperspherical adiabats from the RLU calculations. Ohsaki and Nakamura[14] emphasized the power of the hyperspherical coordinate system to understand the reaction dynamics, and to make more transparent the reaction mechanism. For instance, the wells on the curves correlating to the product channels in the asymptotic limit may result in resonances.

4.2. Reaction Probabilities. Cumulative reaction probabilities $N(E, J = 0)$, CRPs, as a function of energy in the range 0.23−5.80 kcal mol^{-1} are plotted in Figure 2. The CRP results show a dense resonance structure, associated with the well in the exit channel of the PES. Moreover, since the vibrationally adiabatic ground-state threshold energy is lower than zero for this reaction,[9] $\Delta H^{\ddagger}(0\ K) = -0.07$ kcal mol^{-1}, the tunneling contribution is negligible. Oscillations in the reaction probabilities, but not nearly as pronounced as ours, were also found by Zhang et al.[3] and by Li[4] using their time-dependent SVRT model on two PESs, which are both different from our PES. We expect that averaging the reaction probabilities obtained in

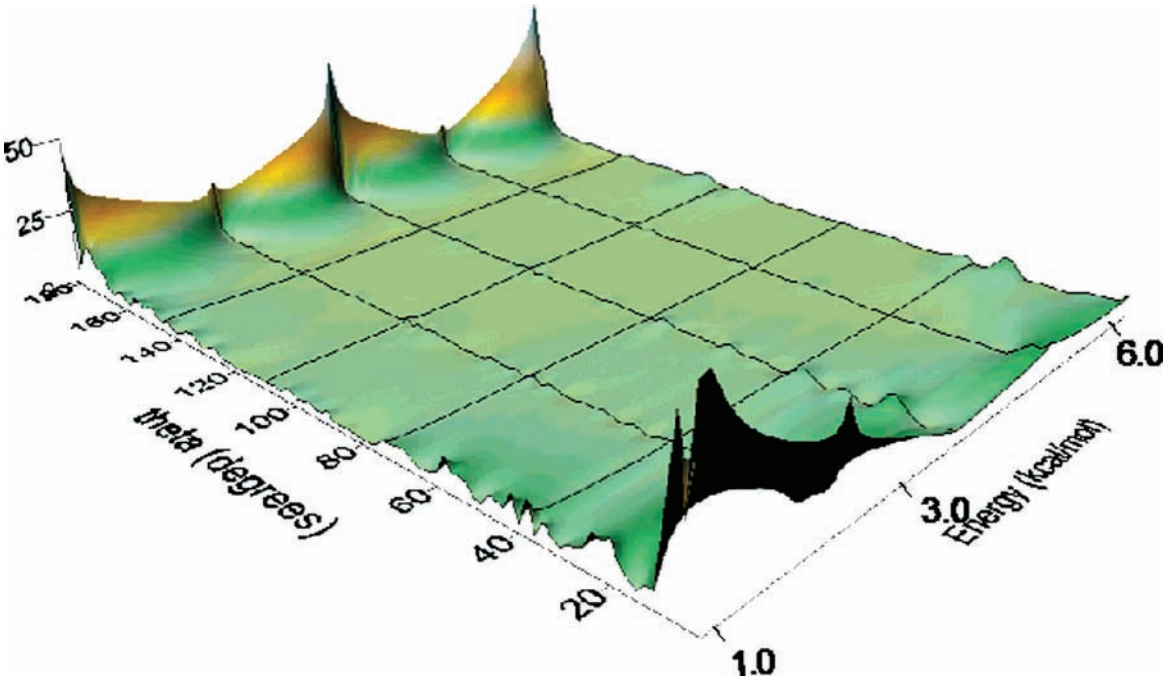

Figure 5. Three-dimensional representation of the state-to-state differential cross sections for ground-state reactants forming FH(v′ = 3) + CH_3(v′ = 0) as a function of collision energy in the range 1.0−6.0 kcal mol^{-1}.

RLU calculations over various orientations would markedly decrease the oscillatory pattern. This would be in line with the SVRT model giving smaller oscillations, as that model averages over orientational degrees of freedom.

Although the oscillations, which are characteristic of resonances, are present in the CRP (Figure 2), it is usual to find that averaging over the partial waves removes these oscillations. We indeed find this behavior when the reaction cross section is considered (Figure 3), although it still shows some of the effects of the resonance signatures, especially the peak at 1.38 kcal mol^{-1}, associated with the FH($\nu = 3$) + CH_3($\nu = 0$) product state. The peak at 3.0 kcal/mol is related to the opening up of a new product state FH($\nu = 3$) + CH_3($\nu = 1$). We note that the cross sections presented are not absolute cross sections and their magnitudes can therefore not be directly compared to experiment or other calculations.

The excitation function (reaction cross section versus collision energy) was measured experimentally by Shiu et al.[15] for the energy range 0.48 to 7.3 kcal mol^{-1} for the formation of ground-state CH_3($\nu' = 0$). This function shows a steep increase from the threshold up to a collision energy of ≈2 kcal mol^{-1}, and then it decays as the collision energy increases. This behavior differs notably from those for the analogous F + H_2 reaction,[16−18] and the isotopic F + CD_4 reaction.[19] Previous QCT calculations[9] on PES-2006 did not reproduce the experimental behavior, rather they showed a gradual increase as the energy was increased. However, when QM calculations are performed on the same surface and ground-state CH_3($\nu = 0$), as in the present paper, the experimental behavior is reproduced, with a maximum value at an energy of 2.1 kcal mol^{-1}.

4.3. Differential Cross Section. The differential scattering dynamics of the title reaction was determined experimentally by Harper et al.[20] via high-resolution IR laser dopplerimetry at a collision energy of 1.8 kcal mol^{-1}. They find for the FH($\nu' =$ 1) and FH($\nu' = 2$) states a clear propensity for forward/backward, $|\cos(\theta)| \approx 1$, versus sideways scattering, $|\cos(\theta)| \approx 0$, although unfortunately the forward versus backward scattering cannot be well characterized, due to experimental difficulties.

Previous QCT vibrationally state resolved FH(ν') scattering angular distributions[9] on PES-2006 at a collision energy of 1.8 kcal mol^{-1} showed that while for the FH($\nu' = 0$) state the sideways distribution dominates over the forward/backward, for all other FH($\nu' = 1,2,3$) states the forward/backward scattering dominates over the sideways, in agreement with experiment. Moreover, as the vibrational state increases, FH($\nu' = 1 \rightarrow \nu' = 3$), the scattering becomes increasingly forward-directed. This result for the FH($\nu' = 3$) state agrees with the experimental data for the analogous F + H_2 → FH ($\nu' = 3$) + H reaction,[21] and with the behavior of the title reaction at high impact parameters, called peripheral reactions by Kornweitz et al.[22]

The reduced dimensionality QM scattering calculations give the FH($\nu' = 3$) state as the most populated, one unit hotter than experiment and QCT results. A reason for this may be that the QM calculations are performed in reduced dimensionality, leaving fewer degrees of freedom to share the available energy. Therefore for the QM results we show results for FH($\nu' = 3$). The QM angular distribution on PES-2006 at a collision energy of 1.8 kcal mol^{-1} is plotted in Figure 4 for the FH($\nu' = 3$) + CH_3($\nu' = 0$) state. Clearly, the forward/backward scattering dominates over the sideways, reproducing the QCT and the experimental results.

In order to shed more light on this problem, in a previous QCT paper[9] we analyzed the evolution of the angular distribution as a function of the collision energy, on the basis of a three-dimensional plot of the differential cross section (DCS)−collision energy (Ecoll)−scattering angle (θ), for the most populated FH($\nu' = 2$) state. A notable change of DCS with collision energy was observed. At low energies, the DCS is practically sideways, but as the energy increases forward scattering dominates, with sudden changes at energies of 2.5 and 3.5 kcal mol^{-1}. This pattern is reminiscent of a resonance signature and supports the experimentally inferred resonance reported by Shiu et al. for this reaction.[1] However, the QCT results need to be taken with caution because of their classical nature. Therefore, the DCS−Ecoll−θ three-dimensional representation is reported here by using reduced dimensionality QM calculations based on the RLU approximation (Figure 5) for ground-state reactants forming the $FH(\nu' = 3) + CH_3(\nu' = 0)$ state. These QM results also show a notable change of DCS with collision energy. While at low energies the DCS is forward/backward, with the backward scattering dominating as the energy increases. Shiu et al.[1] suggested that the mechanism for this possible resonance is a Feshbasch resonance due to dynamical trapping in wells on the vibrationally adiabatic PES. In fact, in a previous paper using PES-2006 we found[9] first, a deep well in the exit channel on the vibrationally adiabatic curve, stabilized by 3.03 kcal mol^{-1} with respect to the products, that supports a quasi-bound complex, and second that this resonance can be assigned to the CH_3 bending umbrella mode.

5. Conclusions

Time-independent reduced dimensionality quantum scattering calculations using the 3D RLU model were performed for the highly exothermic gas-phase hydrogen abstraction reaction $F(^2P) + CH_4 \rightarrow FH(\nu') + CH_3$. In the RLU model the forming F−H bond, the breaking C−H bond, and the CH_3 umbrella motion are treated explicitly. An analytical potential energy surface, PES-2006, which is symmetric with respect to the permutation of the four hydrogen atoms in methane, was used. The surface approximately includes the zero-point energies for the vibrational modes not explicitly treated in the RLU model, and the coupled channel equations were solved in hyperspherical coordinates in the coupled states (J_z-conserving) approximation.

The calculated excitation function for the $CH_3(\nu' = 0)$ state shows a steep increase from the threshold up to a collision energy of 2.1 kcal mol^{-1}, and then it decays as the collision energy increases, reproducing the experimental information by Shiu et al.,[15] and notably improving the QCT results previously reported[9] on the same PES, which strongly contrast with experiment.

The wells found in the hyperspherical adiabats and the oscillations found in the cumulative and state-to-state reaction probabilities suggest scattering resonances, associated with dynamical trapping in a 3.03 kcal mol^{-1} deep well on the vibrationally adiabatic surface in the exit channel.

Finally, state-to-state differential cross sections (DCS) were calculated and compared to experiment and previous QCT calculations. For the $F + CH_4(\nu = 0) \rightarrow FH(\nu' = 3) + CH_3(\nu' = 0)$ reaction and a collision energy of 1.8 kcal mol^{-1}, the DCS shows a forward/backward predominance, in agreement with both experiment and QCT results. In addition, a notable change of DCS with collision energy was observed, changing from forward/backward at low energies to backward scattering as the energy increases. This fact, together with the observation of oscillations in the CRP and state-to-state reaction probabilities, reinforces the existence of scattering resonances for the title reaction.

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