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Resonance Features in the Isotopic Branching Ratios for the F + HD Reaction[†]

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Quantum mechanical cross sections for the two channels of the F + HD reaction, calculated and published by Zhang et al. (*J. Chem. Phys*. **2000**, *112*, 9802) employing the potential energy surface of Stark and Werner (*J. Chem. Phys.* **1996**, *104*, 6515) were used to calculate ratios of cross sections and ratios of rate constants under a variety of initial conditions. It is shown that, for the range of low collision energies at a rotational temperature of 50 K for which a resonance peak for the HF + D product channel was observed by Skodje et al. (*J. Chem. Phys.* **2000**, *112*, 4536; *Phys. Rev. Lett.* **2000**, *85*, 1206), both experimentally and theoretically, and even more so for higher rotational temperatures, there are obvious advantages in presenting results in terms of ratios of cross sections, rather than in terms of absolute cross sections. Results for ratios of cross sections for collision energies higher than the low-energy range of the resonance peak, as well as for ratios of rate constants over a wide temperature range, are presented and discussed.

1. Introduction

The study of the F + H_2 reaction is of central importance to the development of theories in chemical dynamics.[1,2] Numerous experimental and theoretical studies of this reaction and of its isotopic variants F + D_2 and F + HD have been carried out in recent years. Comparisons between theoretical predictions based on various potential energy surfaces (PESs) and experimental measurements have led to conclusions concerning the accuracy of these surfaces. The ab initio PES developed by Stark and Werner (SW PES)[3] is considered to be the most accurate surface available today.[1,2,4] In fact, quantum mechanical (QM) calculations on this PES have led to a nearly quantitative agreement with the photodetachment spectrum of the FH_2^- ion,[5] thereby demonstrating the accuracy of this surface in the transition state region. Other experimental measurements, such as the determination of rate constants for the F + H_2 and F + D_2 reactions and of their ratio (kinetic isotope effect), were also reproduced quite well by QM calculations on this PES, especially near room temperature.[6] However, there are some discrepancies between results of scattering experiments and QM calculations for the F + H_2 reaction,[7,8] and even more so for the F + HD reaction.[4] Significant discrepancies also exist with respect to the intramolecular kinetic isotope effect for the F + HD reaction at low temperatures.[9]

The isotopomeric reaction F + HD is of special interest due to the fact that the F atom can attack either of the two ends of the HD molecule, thus leading to a sampling of different regions of the PES. The two channels are

$$\mathrm{F + HD \rightarrow HF + D} \quad (1a)$$

$$\mathrm{F + DH \rightarrow DF + H} \quad (1b)$$

QM calculations of integral cross sections for the two channels of the F + HD($v = 0$, $j = 0$) reaction employing the SW PES were carried out by Baer[10] for four low collision energies in the range of 0.48−1.40 kcal/mol. He showed that, for the lowest collision energies in this range, the cross sections for the HF + D product channel, σ(HF), are much larger than the cross sections for the DF + H product channel, σ(DF). This large isotopic branching ratio was attributed by him to the existence of a significant tunneling process for the HF + D product channel, but not for the DF + H product channel, because of the thin barrier of the SW PES, which enables the H atoms to tunnel through it almost freely but severely limits the passage of D atoms. This thin barrier was calculated in an earlier publication by Rosenman et al.[6] in which results of QM calculations for the F + H_2 and F + D_2 reactions were presented and discussed.

A combined experimental and theoretical study of integral cross sections as a function of collision energy at a low temperature (50 K) for the reaction of F atoms with HD was carried out by Skodje et al.[11,12] In this study too, very different behaviors for the two channels of this reaction were found by the experimental measurements, as well as by the QM calculations, which were based on the SW PES. For the DF + H product channel, the behavior was found to be essentially classical, with a direct over-the-barrier mechanism. On the other hand, it was found that the HF + D product channel, at very low collision energies, is dominated by tunneling through the barrier. Whereas the cross section increases monotonically with collision energy for the DF + H product channel, for the HF + D product channel, a peak is observed near a collision energy of 0.5 kcal/mol. This peak is observed experimentally and is reproduced quite well by the QM calculations, although the calculated peak is about 2 times higher than the measured peak and slightly shifted to higher collision energies (by about 0.1 kcal/mol). The QM calculations showed that this peak is due to HD ($j = 0$). A much smaller peak, at a lower collision energy, is obtained for HD ($j = 1$). Such peaks for the rotational states $j = 0$ and $j = 1$ were also obtained by the QM calculations of Zhang et al.,[9] also employing the SW PES. On the other hand,

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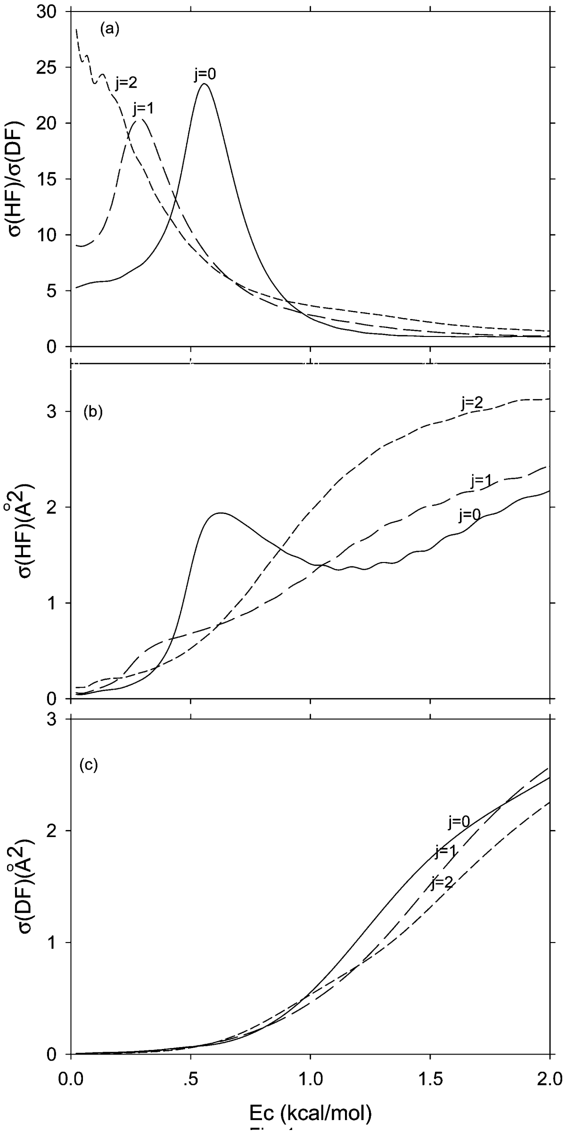

Figure 1. Cross sections and ratios of cross sections, as a function of collision energy, for the two channels of the reaction F + HD (j = 0−2). (a) Isotopic branching ratio σ(HF)/σ(DF), (b) σ(HF), (c) σ(DF).

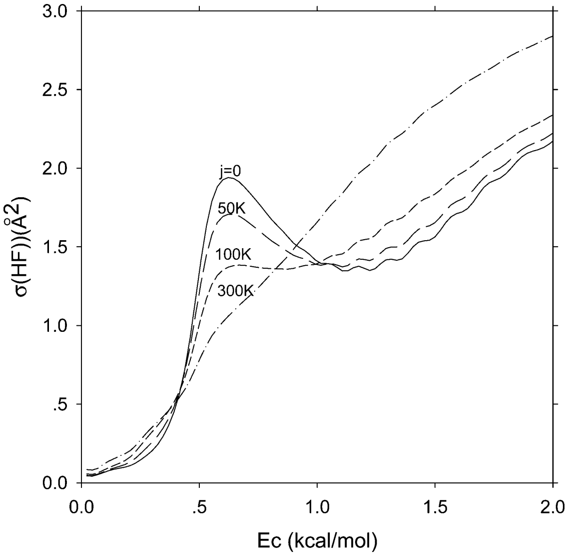

Figure 2. Cross sections σ(HF), as a function of collision energy, for the reaction F + HD for HD (j = 0) and for the rotational temperatures 50,100 and 300 K.

quasiclassical calculations on the same PES[13] did not show any peak. The fact that the QM peak is higher than the experimental peak was attributed by Skodje et al.[11,12] to deficiencies in the PES. They suggested that the barrier of the SW PES might be somewhat too narrow, causing excessive tunneling, or it might be somewhat too low, because of the neglect of spin−orbit coupling.

The main motivation of this study was the outstanding achievement of Skodje et al.,[11,12] who observed a resonance in the integral cross sections for the HF + D product channel of the F + HD reaction at low collision energies. This is the first case in which conclusive experimental evidence was presented for the existence of a reactive resonance in integral cross sections, surviving the effect of partial wave averaging. The purpose of the present study was to determine whether one might expect to observe resonance features under conditions other than those of the experiments of Skodje et al.[11] and whether there is another manner of presenting the results through which the resonance features would be more prominent. To achieve this goal, we carried out calculations of ratios of integral cross sections for the two channels of the F + HD reaction under a variety of initial conditions. These calculations are based on the QM cross sections, as a function of collision energy and of the rotational state of the HD molecule, that were reported by Zhang et al.[9] Our results demonstrate that, for the purpose of looking for resonance peaks, there are advantages in presenting experimental and theoretical results in terms of ratios of cross sections for the two channels of the F + HD reaction, rather than in terms of absolute cross sections for the HF + D product channel. Our results show that, with such a presentation, the resonance peak at low collision energies is significantly more pronounced and should be clearly observed even under conditions where the peak in the cross sections for the HF + D product channel is very small. Results of calculated ratios of cross sections and rate constants for the two channels of the F + HD reaction under a variety of initial conditions other than the experimental conditions of Skodje et al.[11] are also presented and discussed.

2. Results and Discussion

2.1. Isotopic Branching Ratios σ(HF)/σ(DF). The calculations reported here are based on the QM cross sections, as a function of the collision energy and of the initial rotational state of the HD molecule, reported by Zhang et al. (Figures 1 and 3 of ref 9). In their calculations, they employed the SW PES. Figure 1 of the present study shows the absolute cross sections, σ(HF) and σ(DF), for the HF + D and DF + H product channels, respectively, and ratios of cross sections, σ(HF)/σ(DF), as a function of collision energy for the initial rotational states j = 0−2. Smooth behavior is observed for σ(DF) for all initial rotational states (Figure 1c). For σ(HF) (Figure 1b), a peak is observed for j = 0 at a collision energy of 0.63 kcal/mol, and a much smaller peak is observed for j = 1 at a collision energy of 0.30 kcal/mol. No peak is observed for j = 2. This is consistent with the QM results of Skodje et al. (Figure 3 of ref 11). Significantly more pronounced peaks for j = 0 and j = 1 are observed in Figure 1a where isotopic branching ratios, σ(HF)/σ(DF), are presented. A comparison between parts a and b of Figure 1 clearly demonstrates the advantage of presenting the results in terms of isotopic branching ratios, rather than absolute cross sections.

Figure 2 shows integral cross sections σ(HF) as a function of collision energy for HD at the rotational temperatures 50,

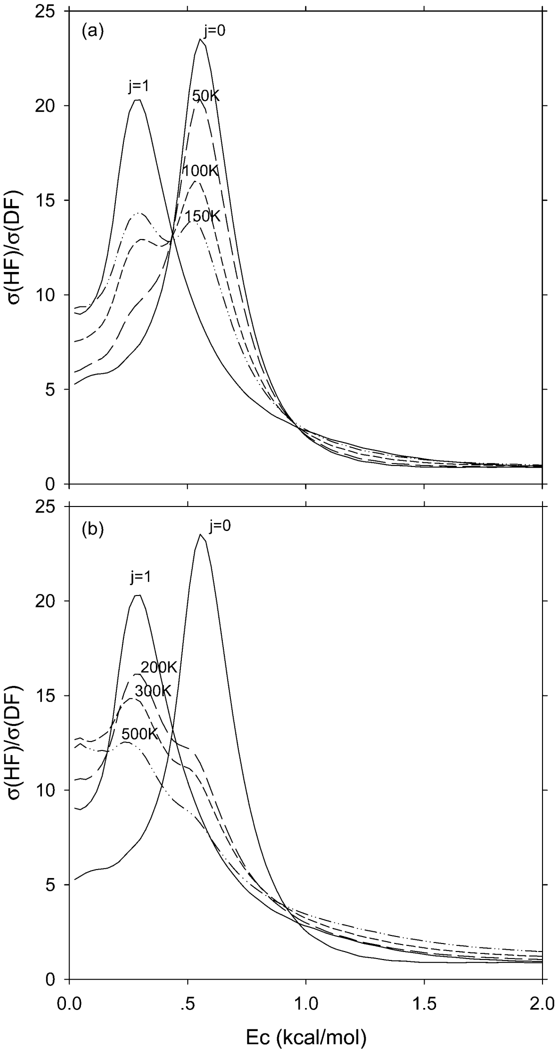

Figure 3. Isotopic branching ratios, σ(HF)/σ(DF), as a function of collision energy for the reaction F + HD for HD ($j = 0$ and 1) and for the various rotational temperatures (a) 50, 100, and 150 K; (b) 200, 300, and 500 K.

TABLE 1: Distribution of Rotational States of HD at Various Temperatures

	fraction of molecules in state j					
T (K)	$j = 0$	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$
50	0.80	0.20				
100	0.51	0.43	0.06			
150	0.36	0.47	0.15	0.02		
200	0.22	0.57	0.17	0.04		
300	0.20	0.39	0.28	0.11	0.02	
500	0.12	0.28	0.28	0.19	0.09	0.03

100, and 300 K, as compared to the cross sections for HD in rotational state $j = 0$. The distributions of rotational states at these temperatures, as well as for some other temperatures, are presented in Table 1. For a temperature of 50 K, corresponding to the conditions of the experiments of Skodje et al.,[11] 80% of the HD is in the rotational state $j = 0$, and a pronounced peak is observed. As the temperature is raised, the contribution of this state becomes smaller, and correspondingly, the size of the peak decreases. No significant peak due to $j = 1$ is observed at any of the three temperatures.

Figure 3 shows the isotopic branching ratio σ(HF)/σ(DF) as a function of collision energy for six temperatures in the range 50−500 K. In the upper part of the figure, the results for 50, 100, and 150 K are presented. Two peaks are observed, corresponding to $j = 0$ and $j = 1$. In this temperature range, the percentage of HD in the $j = 0$ state decreases from 80 to 36%, and the percentage of HD in the $j = 1$ state increases from 20 to 47%; correspondingly, the peak due to $j = 0$ decreases, and the peak due to $j = 1$ increases. In the lower part of the figure, results are presented for 200, 300, and 500 K. In this temperature range, the percentage of HD in the $j = 0$ state decreases from 22 to 12%, and the peak due to this state decreases and almost disappears. The percentage of HD in the $j = 1$ state also decreases, from 57 to 28%, and the peak due to this state also decreases, but a very small peak is observed even at 500 K.

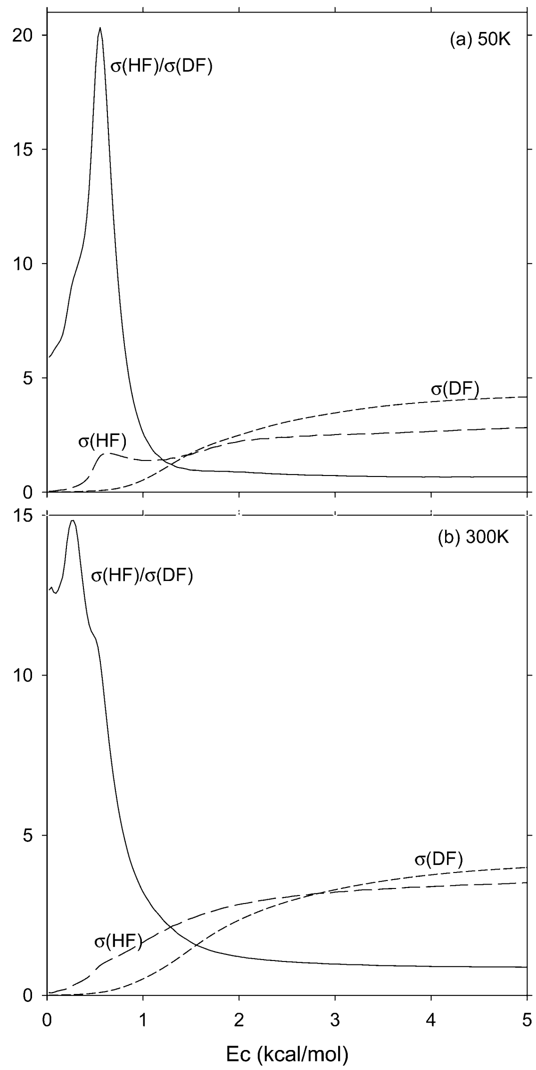

Figure 4. Cross sections (in units of Å^2) and ratios of cross sections, presented on the same scale, as functions of collision energy for the rotational temperatures (a) 50 and (b) 300 K.

A comparison between Figure 3 and Figure 2 demonstrates again that, for the purpose of observing resonance peaks due to tunneling, it is preferable to present results in terms of isotopic branching ratios, rather than in terms of absolute cross sections. Whereas in Figure 2 only the peak due to $j = 0$ is observed and it disappears almost completely at 300 K, in Figure 3, two peaks, due to $j = 0$ and $j = 1$, are observed. The peak due to $j = 1$ is clearly observed even at 300 K and higher. This is even clearer from Figure 4, where σ(HF) and σ(HF)/σ(DF) are presented as functions of the collision energy on the same scale for temperatures of 50 and 300 K. As can be seen from this figure, for 50 K, the peak in the isotopic ratio σ(HF)/σ(DF)

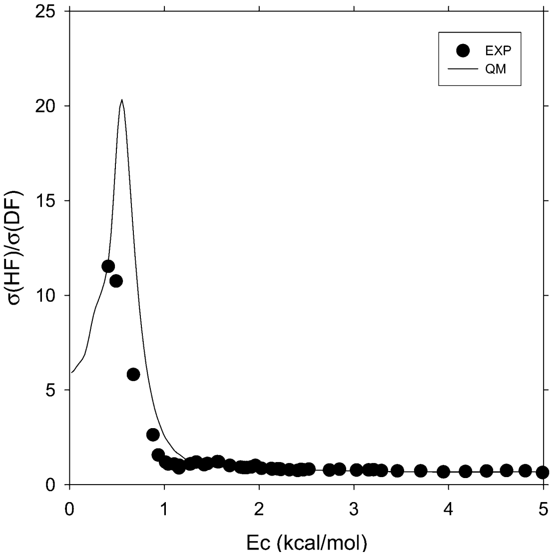

Figure 5. Isotopic branching ratios, σ(HF)/σ(DF), as a function of collision energy, for the reaction F + HD at 50 K. Filled circles, experimental results of ref 11; solid line, QM results of the present study.

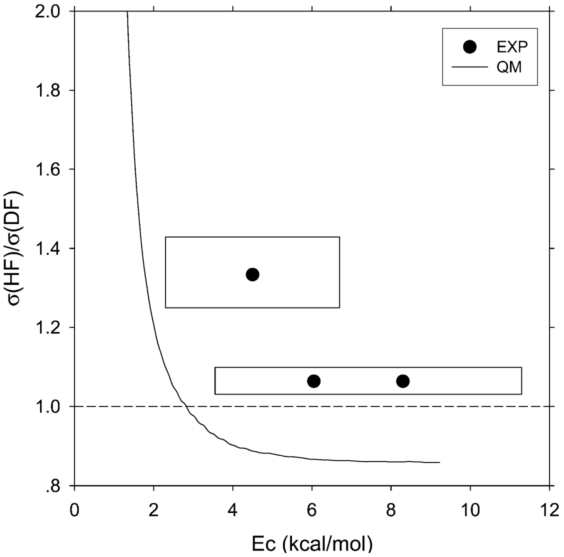

Figure 6. Isotopic branching ratios, σ(HF)/σ(DF), as a function of collision energy, for the reaction F + HD at 300 K. Filled circles, experimental results of ref 14 (the boxes account for the errors in the branching ratios and in the collision energies); solid line, QM results of the present study.

due to $j = 0$ is more than 10 times higher than the peak in σ(HF) and is much sharper. For 300 K, a small peak due to $j = 1$ is observed for σ(HF)/σ(DF), whereas the curve for σ(HF) is apparently smooth. Experiments to test the behavior shown in Figures 3 and 4 would involve careful measurements of branching ratios σ(HF)/σ(DF) in the very low collision energy range 0−2 kcal/mol for some rotational temperatures up to 300 K. Although such experiments would probably be rather difficult because of the low cross sections in this energy range, especially for the DF + H products channel, they would be very important as a test of the accuracy of the SW PES.

The experimental isotopic branching ratios σ(HF)/σ(DF) determined by Skodje et al.[11] at 50 K for the range of collision energies 0−5 kcal/mol are compared with calculated results in Figure 5. Unfortunately, only part of an experimental peak is observed, as only a few measurements have been carried out in the low-collision-energy range, especially measurements of σ(DF). However, the shift of the theoretical peak to higher collision energies with respect to the experimental peak reported by Skodje et al.[11] is clearly observed. The good agreement between experiment and theory in the higher-energy range, for which most of the measurements were made, is also observed. More careful measurements are needed in the low-energy range for a better comparison between experiment and theory in this important range. It should be noted that, when the experimental results are presented in terms of isotopic branching ratios, there is no need to include a normalization factor, which is essential in the presentation of absolute cross sections in comparison with theoretical predictions.[11,12] This is another advantage of such a presentation.

Measurements at a much higher rotational temperature than that used in the experiments of ref 11 were carried out by Johnston et al.[14] They measured the isotopic branching ratio σ(HF)/σ(DF) at 300 K for three collision energies, namely, 4.50 ± 2.20, 6.05 ± 2.50, and 8.30 ± 3.00 kcal/mol. The results are presented in Figure 6, in comparison with the QM results calculated in the present study. It can be seen that the calculated isotopic branching ratios are significantly lower than the measured ratios over the whole energy range of the experiments. For collision energies higher than 2.8 kcal/mol, the calculated ratios are lower than unity, whereas the measured ratios are higher than unity. This is probably due to some inaccuracies in the SW PES. This discrepancy cannot be related to too much tunneling included in the calculations, because in this case, the calculated results would be higher than the experimental results, rather than lower. Moreover, under the conditions of the experiments of Johnston et al.,[14] tunneling is probably not very important. As noted by Skodje et al.,[11] the SW PES is quite accurate in the collinear portion, and therefore, the calculated cross sections for low rotational states, especially $j = 0$, agree quite well with the experimental results (Figure 5). However, other portions of the PES are probably less accurate, and therefore, at higher rotational states and especially at high collision energies, there are discrepancies between the calculated cross sections and the experimental results (Figure 6).

2.2. Intramolecular Kinetic Isotope Effect, k_{HF}/k_{DF}. Zhang et al.[9] calculated the intramolecular kinetic isotope effect, k_{HF}/k_{DF}, as a function of temperature and compared the results with experimental results of one of the authors of the present publication[15] for the temperature range of 159−413 K. They found that the calculated values are higher than the experimental values by a factor of about 2 in the lowest temperature and approach the measured values at the highest temperature. The calculated and experimental results are presented in Figure 7. Also presented in this figure are the quasiclassical trajectory results of Aoiz et al.[13] As can be seen, whereas the quasiclassical results underestimate the kinetic isotope effect, the QM results overestimate the effect, and the discrepancy increases as the temperature is lowered. This indicates that the tunneling effect included in the QM calculations is probably too high. This conclusion is consistent with the suggestion of Skodje et al.[11,12] that the barrier of the SW PES might be somewhat too narrow.

Calculated kinetic isotope effects, $k_{HF}/k_{DF,}$ over a very wide temperature range, down to 10 K, for HD in the rotational states 0−2, and for thermal distributions of rotational states are presented in Figure 8a. Individual rate constants, k_{HF} and k_{DF}, for thermal distributions of rotational states, are presented in Figure 8b. As can be seen in Figure 8a, peaks are observed in the curves for $j = 0$ and $j = 1$, but not for $j = 2$. A peak is also observed in the curve for the thermal distributions of rotational states, and this curve is very close to the curve for $j = 0$. This

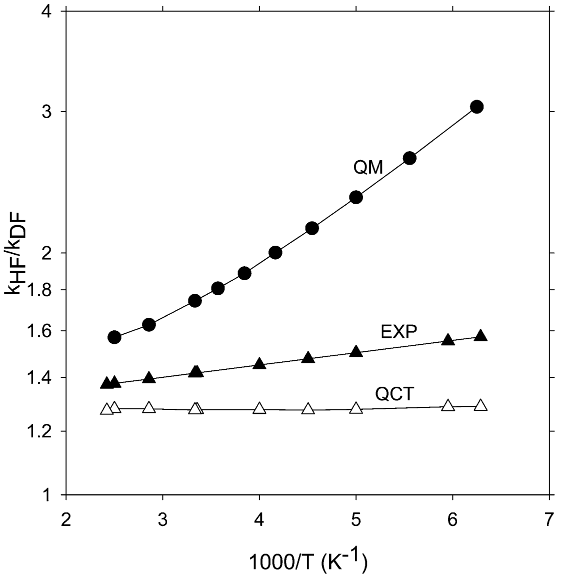

Figure 7. Intramolecular kinetic isotope effects, k(HF)/k(DF), as a function of 1000/T for the reaction F + HD. Filled triangles, experimental results of ref 15; empty triangles, quasiclassical trajectory results of ref 13; filled circles, QM results of ref 9.

is because most of the HD molecules at temperatures near the maximum of the peak of this curve (60 K) and at lower temperatures are in the $j = 0$ state. The peaks observed in Figure 8a result from the resonance peaks in the curves for σ(HF)/σ(DF) as a function of collision energy (Figures 1a and 3), but they are rather wide (they spread over a wide range of temperatures), because of the effect of averaging over thermal distributions of collision energies involved in the calculations of rate constants. No peak is observed in Figure 8a for $j = 2$, as there is no resonance peak for this rotational state in the curve for σ(HF)/σ(DF). It can also be seen that, whereas there is a peak in the curve for k_{HF}/k_{DF} for thermal distributions of rotational states (Figure 8a), there is no peak in the corresponding curve for k_{HF} (Figure 8b). This is probably due to the fact that the resonance peak for σ(HF) is much smaller than the peak for σ(HF)/σ(DF) (Figure 4) and is washed out altogether by the Boltzmann averaging over collision energies in the calculations of rate constants.

Balakrishnan and Dalgarno[16] investigated the isotopic branching ratios and the intramolecular kinetic isotope effects for the F + HD reaction at ultracold temperatures. Their calculations, which were also based on the SW PES, showed that, in the limit of zero temperature, the value of the intramolecular kinetic isotope effect, k_{HF}/k_{DF}, is 5.5. The same value was obtained in the present study for the lowest temperature of the calculations.

3. Summary

The main purpose of the present study was to investigate whether one might expect to observe resonance features in the integral cross sections for the F + HD reaction under conditions that are different from the experimental conditions of Skodje et al.[11] and whether results can be presented in a different manner, so that such features will be more pronounced. To achieve this goal, calculations of isotopic branching ratios, σ(HF)/σ(DF), and of intramolecular kinetic isotope effects, k_{HF}/k_{DF}, under a variety of initial conditions were carried out. The calculations are based on the QM cross sections for the two channels of this reaction for the SW PES reported by Zhang et al.[9] It is shown that, for the purpose of observing resonance peaks, there are obvious advantages in presenting the results in terms of isotopic branching ratios, σ(HF)/σ(DF), rather than in terms of absolute cross sections, σ(HF). With such a presentation, the resonance peaks are much sharper and are much larger than they are for σ(HF) under the same conditions, and they are clearly observed even under conditions where no peaks are observed for σ(HF). Another advantage is that no normalization factor is needed when the experimental results are compared to theoretical results, whereas such a normalization is needed when the results are presented in terms of σ(HF).[11,12] It is also shown that the resonance features survive even the effect of averaging over the thermal distributions of collision energies involved in the calculations of rate constants. Peaks, though rather wide, are observed in the curves presenting k_{HF}/k_{DF} as a function of 1000/T for HD in rotational states 0 and 1 and also for thermal distributions of rotational states. On the other hand, the resonance peak for σ(HF) does not survive this averaging process, and the corresponding curve for k_{HF} is rather smooth. Experimental studies based on the results of our calculations, although probably rather difficult, would be very important as a test of the accuracy of the SW PES.

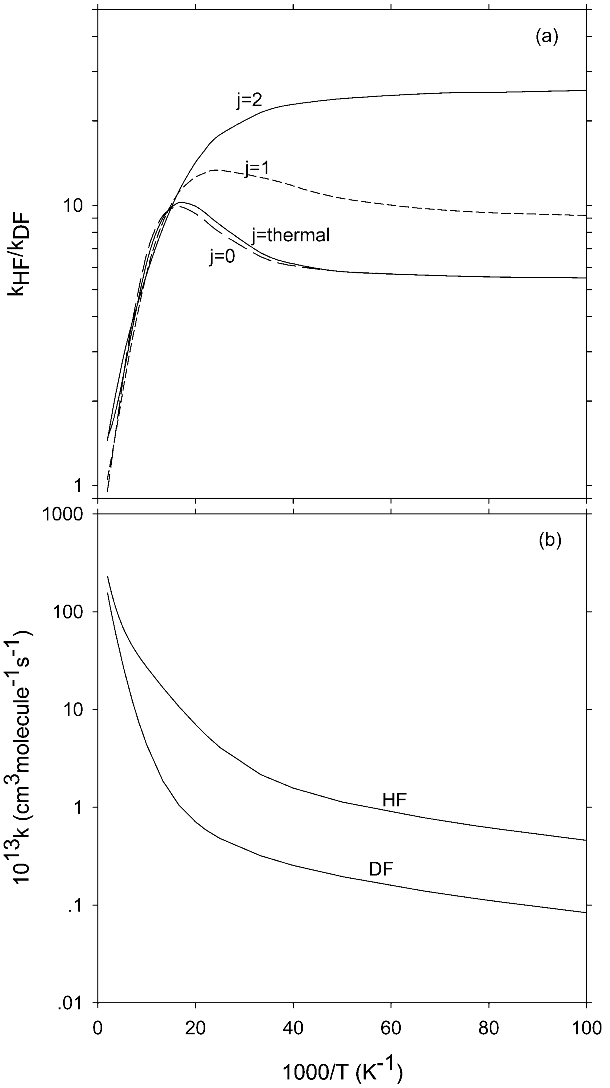

Figure 8. Rate constants and ratios of rate constants for the two channels of the F + HD reaction, as a function of 1000/T. (a) k_{HF}/k_{DF} for HD in the rotational states 0−2 and for thermal distributions of rotational states; (b) k_H and k_D for thermal distributions of rotational states.

Isotopic branching ratios, σ(HF)/σ(DF), calculated under the conditions of the experiments of Johhston et al. (300 K and collision energies in the range of 4.5−8.3 kcal/mol)[14] were found to be significantly lower than the experimental results. This is probably due to some inaccuracies in the SW PES.

As indicated here and in some other studies, there are some discrepancies between results of QM calculations based on the SW potential energy surface, which is the most accurate surface available today for the F + H_2 system, and experimental results. Some slight modifications of this potential energy surface are needed to close the gaps that still exist between experimental and theoretical results for this system.

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