140 *J. Phys. Chem. A* **2004,** *108,* 140−145

# Quasiclassical Trajectory Calculations for the Reactions F + HCl, F + HBr, and F + HI

**Haya Kornweitz**[†,‡] **and Avigdor Persky***[,†]

*Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel, and The College of Judea and Samaria, Ariel 44837, Israel*

*Received: June 12, 2003*

LEPS potential energy surfaces were constructed for the reactions F + HCl, F + HBr, and F + HI so as to reproduce the available experimental kinetic data and data concerning the energy distribution among products as well as possible. Calculations were carried out by the quasiclassical trajectory method. The results are discussed in comparison with available experimental results as well as with results of calculations from other research groups. In general, good agreement with experiment is obtained. This agreement is better than the agreement obtained for the other calculations carried out until now for these reactions.

## 1. Introduction

The reactions of fluorine atoms with hydrogen halides

$$\mathrm{F + HCl \rightarrow HF + Cl} \qquad \Delta H_0^{\,0} = -32.8 \text{ kcal/mol} \quad (1)$$

$$\mathrm{F + HBr \rightarrow HF + Br} \qquad \Delta H_0^{\,0} = -48.5 \text{ kcal/mol} \quad (2)$$

$$\mathrm{F + HI \rightarrow HF + I} \qquad \Delta H_0^{\,0} = -64.7 \text{ kcal/mol} \quad (3)$$

belong to the group of reactions of the type heavy + light− heavy which are of much interest in molecular dynamics. Furthermore, these reactions are of importance in relation to chemical lasers, since they have very low energy barriers, are very exothermic, and the HF product is formed highly vibrationally excited. Experimental studies of these reactions, which were reported in the literature, include the determination of the energy partitioning among reaction products,[1−8] especially the distribution of the vibrational states of the HF and kinetic studies,[9−17] most of them at room temperature.

Various experimental methods were used in the studies of the vibrational distribution of the product HF in reactions 1−3.[1−8] In all these studies, except for the study by Polanyi and co-workers of reaction 2,[7] population inversion of the vibrational states of the HF was found. The results of ref 7 are exceptional as they indicate a nearly statistical distribution of the vibrational states.

Most of the kinetic experiments of reactions 1−3 were carried out only at room temperature.[1,5,6,9−13,15] Only in very few experiments has the temperature dependence of rate constants been determined. Würzberg and Houston[14] found a non-Arrhenius temperature dependence for all three reactions. Moore et al.[16] studied the temperature dependence for the F + HCl reaction and found that the rate constant is independent of temperature over a wide temperature range. Kinetic studies of the reaction F + HBr and of its isotopic analogue F + DBr have been carried out in our laboratory.[17,18] In both cases, a linear Arrhenius dependence over a wide temperature range was obtained, in contrast to the results of Würzberg and Houston.[14] It should be noted that a linear dependence was also obtained in our laboratory for the similar reaction Cl + HBr.[19]

Very few theoretical calculations concerning the kinetics and the energy partitioning among products for reactions 1−3 have been reported in the literature and most of them are for the F + HCl reaction. In two of the studies of the F + HCl reaction,[2,3] the quasiclassical trajectory (QCT) method was used employing LEPS potential-energy surfaces. In three other studies, an ab initio potential-energy surface, which was developed by Sayós et al.,[20] was employed for variational transition-state theory,[20] time-dependent quantum wave packet,[21] and QCT[22] studies. To the best of our knowledge, the only study concerning the two other reactions was carried out by Beadle et al.[2] by the QCT method, using LEPS potential-energy surfaces.

In this study, semiempirical LEPS potential-energy surfaces were developed so as to fit, as well as possible, the available experimental results for reactions 1−3. The QCT method was used in the calculations. The results are presented and discussed in comparison with the available experimental and theoretical data.

## 2. Potential-Energy Surfaces and Results

**2.1. Potential-Energy Surfaces and Computational Procedure.** Semiempirical LEPS potential-energy surfaces[23] for reactions 1−3 were constructed so as to reproduce the kinetic data and the energy distribution among the products as well as possible. For each of the three reactions, various combinations of Sato parameters were tested for constructing the potential-energy surfaces. QCT calculations were carried out on these surfaces, and the results were compared with the available experimental data. The sets of parameters, which gave the best agreement with experiment, are presented in Table 1. This table also includes the molecular parameters needed for constructing the surfaces. Contour diagrams of the best potential-energy surfaces for the collinear configuration are shown in Figure 1.

The QCT calculations were carried out for F + HX ($v = 0$, $j$ = thermal distribution). Calculations were performed for different collision energies between 0.001 and 8.0 kcal/mol (these reactions do not have any appreciable threshold). For every collision energy, 5000 trajectories were calculated. The impact parameter $b$ for every trajectory was randomly selected,

---

[*] To whom correspondence should be addressed. E-mail: persky@mail.biu.ac.il.

[†] Bar-Ilan University.

[‡] The College of Judea and Samaria.

10.1021/jp030748e CCC: $27.50 © 2004 American Chemical Society
Published on Web 12/05/2003

**TABLE 1: Parameters of the LEPS Potential Energy Surfaces for the Reactions F + HCl, F + HBr, and F + HI**

| reaction | | $D_e$[a] (kcal/mol) | $\beta$[a] (Å$^{-1}$) | Re[a] (Å) | Sato parameters |
|---|---|---|---|---|---|
| F + HCl | H−F | 141.215 | 2.218 | 0.9168 | 0.20 |
| | H−Cl | 106.59 | 1.868 | 1.275 | −0.03 |
| | F−Cl | 61.21 | 2.310 | 1.628 | 0.23 |
| F + HBr | H−F | 141.215 | 2.218 | 0.9168 | 0.60 |
| | H−Br | 90.43 | 1.809 | 1.4144 | 0.35 |
| | F−Br | 59.72 | 2.211 | 1.7589 | 0.15 |
| F + HI | H−F | 141.215 | 2.218 | 0.9168 | 0.82 |
| | H−I | 73.762 | 1.791 | 1.6041 | 0.26 |
| | F−I | 67.925[b] | 1.965[b] | 1.906[b] | 0.10 |

[a] Reference 25 except for the data for F−I. [b] Reference 2.

according to $b^2$, in the range between 0 and $b_{max} = 5.0$ Å. The results were then integrated over thermal distributions of collision energies to obtain values for rate constants and for energy distributions among the products.

A statistical multisurface factor $G(T)$ was included in the calculations of rate constants

$$G(T) = \frac{1}{2 + \exp(-\Delta E/RT)} \qquad (4)$$

where $\Delta E = 1.16$ kcal mol$^{-1}$.

This factor accounts for the statistical population of the asymptotic $^2P_{3/2}$ and $^2P_{1/2}$ states of F atoms, assuming that nonadiabatic transitions can be neglected (see, for example, refs 21 and 24 and references therein).

**2.2. Rate Constants and Kinetic Isotope Effects.** Calculations for each of the three F + HX reactions were carried out at three temperatures. Calculations were also carried out for the isotopomeric reactions F + DX at 298 K. The calculated rate constants at room temperature are presented in Table 2, where they are compared with available experimental data as well as with results of other calculations. Some of the experimental results presented in Table 2 were obtained by multiplying the measured rates relative to the rate of the F + $CH_4$ reaction by the updated value of $k_{F+CH_4}$ at 298 K, $k_{F+CH_4} = (6.20 \pm 0.50) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[26,27] The rate constant for the F + HBr reaction was measured relative to the rate of the F + $H_2$ reaction.[17] The rate constant $k_{F+HBr}$ was obtained by multiplying the measured ratio $k_{F+HBr}/k_{F+H_2}$[17] by the updated value for $k_{F+H_2}$ at 298 K, $k_{F+H_2} = (2.43 \pm 0.15) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[28] The comparison between our calculated results and the available experimental results presented in Table 2 shows a quite good agreement for all three reactions. The results of Beadle et al.,[2] calculated by the QCT method on LEPS potential-energy surfaces, are very low in comparison with the experiment for all three reactions. It should be noted that Beadle et al. fitted the surfaces only to the experimental energy distribution of the products, without taking into consideration any other experimental data. Three other calculations were carried out for the F + HCl reaction, employing the ab initio potential-energy surface developed by Sayós et al.[20] In these studies, the variational transition-state theory,[20] the time-dependent quantum wave packet,[21] and the QCT[22] methods, respectively, were employed. In the first and third of these calculations, good agreement with experiment was obtained. A somewhat higher result was obtained in the second calculation. It should be noted that a scaling factor was introduced in the ab initio points near the transition state of the potential-energy surface to fit the results calculated by the variational transition-state method to the experimental rate constants of refs 13, 14, and 16 (around $8 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which seems to be close to the correct value).

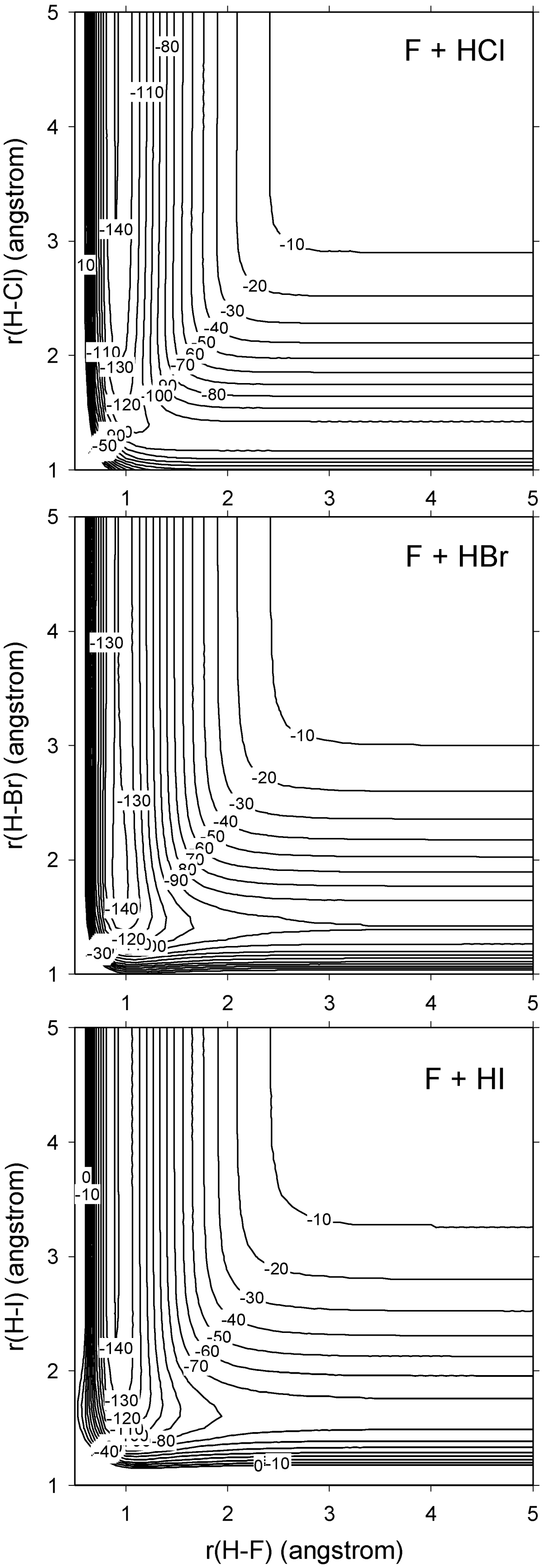

**Figure 1.** LEPS potential-energy surfaces for the F + HX reactions for the collinear configuration. (a) F + HCl; (b) F + HBr; (c) F + HI. The contour lines are in kcal/mol.

The temperature dependence of the rate constants obtained in the present study is presented in Figure 2. The straight lines

**TABLE 2: Rate Constants for the Reactions F + HCl, F + HBr, and F + HI at 298 K**

| investigators | $10^{11}k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) | | |
|---|---|---|---|
| | F + HCl | F + HBr | F + HI |
| Experiments | | | |
| Jonathan et al.[1] (1971)[a] | 1.20 ± 0.15 | 5.4 ± 1.0 | 7.4 ± 0.9 |
| Kompa and Wanner[9] (1972) | 2.5 | | |
| Pollock and Jones[10] (1973)[b] | 1.2 | | |
| Wagner et al.[11] (1976) | 1.1 | | |
| Clyne and Nip[12] (1978) | 1.6 ± 0.6 | | |
| Würzberg et al.[13] (1978) | 0.82 ± 0.09 | 3.30 ± 0.20 | 2.66 ± 0.07 |
| Würzberg and Houston[14] (1980) | 0.81 ± 0.05 | 4.50 ± 0.40 | 4.10 ± 0.08 |
| Sung and Setser[5] (1977)[a] | 0.81 ± 0.14 | 4.2 ± 0.5 | 4.6 ± 0.6 |
| Tamagake et al.[6] (1980)[a] | 0.81 ± 0.14 | 4.0 ± 0.6 | 3.8 ± 0.6 |
| Smith and Wrigley[15] (1981) | 0.70 ± 0.03 | 6.2 ± 0.5 | $5.6^{+0.6}_{-0.2}$ |
| Edrei and Persky[17] (1989)[c] | | 4.1 ± 0.4 | |
| Moore et al.[16] (1994) | 0.72 ± 0.05 | | |
| Calculations | | | |
| Beadle et al.[2] (1978)[d] | 0.051 | 0.046 | 0.040 |
| Sayós et al.[20] (1999)[e] | 0.83 | | |
| Tang et al.[21] (2000)[f] | 1.1(appx.) | | |
| Sayós et al.[22] (2000)[g] | 0.79 ± 0.01 | | |
| This work[d,h] | 0.67 | 3.2 | 3.3 |

[a] Measured relative to the F + $CH_4$ reaction for which the rate constant (6.20 ± 0.50) × $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is taken.[26,27] [b] Measured relative to the F + NO + M recombination chemiluminescence reaction. [c] Measured relative to the F + $H_2$ reaction for which the rate constant (2.43 ± 0.15) × $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is taken.[28] [d] QCT calculations on LEPS potential-energy surfaces. [e] Variational transition-state theory calculation on an ab initio potential energy surface. A multisurface factor of $^1/_3$ was included in the calculations. [f] Time-dependent quantum wave packet calculations on an ab initio potential-energy surface.[20] A statistical multisurface factor of 2/4.3 has been included in the calculations. The approximate value has been estimated from Figure 5b of ref 21. [g] QCT calculations on an ab initio potential-energy surface.[20] A statistical multisurface factor of $^1/_3$ has been included in the calculations. [h] QCT calculations. A statistical multisurface factor of 0.467 (calculated from eq 4) has been included in the calculations.

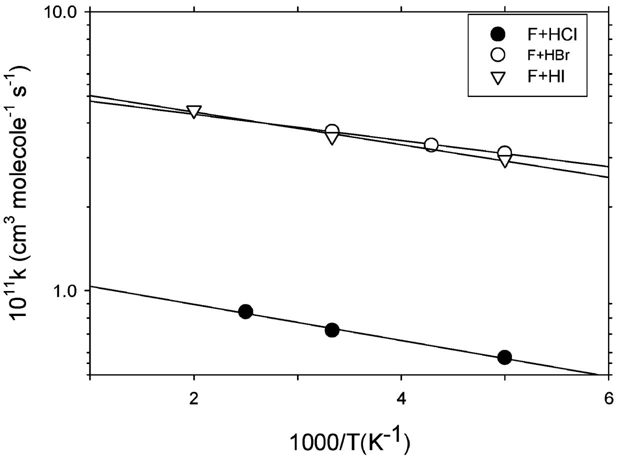

**Figure 2.** Semilogarithmic plots of the calculated rate constants for the F + HX reactions as a function of 1000/*T*. (●) F + HCl; (○) F + HBr; (▽) F + HI.

in this figure correspond to the Arrhenius equations

$$k_{\mathrm{F+HCl}} = 1.0 \times 10^{-11} \exp(-117/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

$$k_{\mathrm{F+HBr}} = 4.5 \times 10^{-11} \exp(-83/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

$$k_{\mathrm{F+HI}} = 4.6 \times 10^{-11} \exp(-96/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

As can be seen from Figure 2, and as could be expected for calculations based on LEPS potential energy surfaces, a linear Arrhenius temperature dependence is obtained for each of the three reactions. The activation energies are low, 0.23, 0.16, and 0.19 kcal/mol for reactions 1, 2, and 3, respectively.

The temperature dependence for the F + HCl reaction was studied experimentally by Würzberg and Houston[14] and by Moore et al.[16] Würzberg and Houston observed a weak temperature dependence below room temperature (194−298 K), with the rate increasing only slightly with increasing temperature, and a much stronger increase above 298 K. Moore et al. carried out experiments in the range 139−296 K and found no temperature dependence in this range. Our calculations, which show a linear dependence and a low activation energy, agree with the experimental results at room temperature and below. We believe that additional experiments should be performed at higher temperatures in order to learn more about the temperature dependence for this reaction.

The temperature dependence for the F + HBr reaction was studied experimentally by Würzberg and Houston[14] and also by us.[17] Würzberg and Houston found an unusual nonlinear Arrhenius temperature dependence, with the rate constant decreasing strongly as the temperature is lowered from 373 to 271 K and then increasing strongly when the temperature is lowered further, down to 195 K. In our experiments, a normal linear temperature dependence was obtained in the range 203−298 K (the rate constant was found to decrease when the temperature was lowered), in contrast to the unusual behavior found by Würzberg and Houston. A linear dependence and a normal behavior was found by us also for the isotopomeric reaction F + DBr in the temperature range 210−298 K[18] and for the reaction Cl + HBr in the temperature range 222−504 K.[19] In our experiments, the rate constant for the F + HBr reaction was measured relative to the rate constant for the F + $H_2$ reaction. The experimental activation energy for the F + HBr reaction was found to be about the same as the activation energy for the F + $H_2$ reaction, which, according to recent evaluations, is 0.90 ± 0.10 kcal/mol[28] or 0.90 ± 0.20 kcal/mol.[29] The value calculated in the present study, 0.16 kcal/mol, is lower than the experimental value. However, both of them indicate a rather weak temperature dependence of the rate constant.

The temperature dependence for the F + HI reaction was studied experimentally only by Würzberg and Houston.[14] The behavior observed in this case is very similar to the behavior found by them for the F + HCl reaction and very different from the behavior found for the F + HBr reaction. The rate constant was found to be independent of temperature in the range 194−293 K and to increase appreciably with temperature above room temperature. Our results, which indicate a linear temperature dependence with a very low activation energy (0.19 kcal/mol), are in good agreement with the experimental results for temperatures below room temperature. We believe that the unusual temperature dependence found by Würzberg and Houston for the F + HI reaction, as well as for the two other reactions F + HCl and F + HBr, may be wrong and is probably due to some experimental difficulties. Additional experiments would be very helpful and important for the research of the dynamics of these reactions.

As indicated above, calculations were carried out also for the isotopomeric reactions F + DX (X = Cl, Br, I) at 298 K. The calculated kinetic isotope effects $k_{\mathrm{F+HX}}/k_{\mathrm{F+DX}}$ at 298 K are presented in Table 3, where they are compared with the available experimental data, as well as with results of other calculations (carried out only for the F + HCl reaction). Kinetic isotope

**TABLE 3: Kinetic Isotope Effects $k_{F+HX}/k_{F+DX}$ at 298 K**

| reaction | research group | $k_{F+HX}/k_{F+DX}$ |
|---|---|---|
| F + HCl | Würzberg et al.[13] (1978)[a] | 1.38 ± 0.29 |
| | Sayós et al.[20] (1999)[b] | 1.70 |
| | Sayós et al.[22] (2000)[b] | 1.81 ± 0.09 |
| | this work[b] | 1.27 |
| F + HBr | Würzberg et al.[13] (1978)[a] | 1.29 ± 0.18 |
| | Schwarz and Persky[18] (1992)[a] | 1.07 ± 0.12 |
| | this work[b] | 1.05 |
| F + HI | Würzberg et al.[13] (1978)[a] | 1.29 ± 0.14 |
| | this work[b] | 1.06 |

[a] Experiments. [b] Calculations.

**TABLE 4: Energy Disposal in the Reactions F + HCl, F + HBr, and F + HI at 298 K**

| reaction | investigators | $f_V$ | $f_R$ | $f_T$ |
|---|---|---|---|---|
| F + HCl | experiments | | | |
| | Jonathan et al.[1] (1971) | 0.58 ± 0.02 | | |
| | Beadle et al.[2] (1978) | 0.52 | 0.21 | 0.27 |
| | Ding et al.[3] (1973) | 0.56 | 0.21 | 0.23 |
| | Tamagake et al.[6] (1980) | 0.51 | 0.18 | 0.31 |
| | QCT[a] | | | |
| | Beadle et al.[2] (1978) | 0.67 | 0.17 | 0.16 |
| | Ding et al.[3] (1973) | 0.55 | 0.25 | 0.20 |
| | Sayós et al.[22] (2000) | 0.71 ± 0.14 | 0.23 ± 0.13 | 0.06 ± 0.04 |
| | this work | 0.58 | 0.26 | 0.16 |
| F + HBr | experiments | | | |
| | Jonathan et al.[1] (1971) | 0.54 ± 0.02 | | |
| | Beadle et al.[2] (1978) | 0.56 | 0.11 | 0.33 |
| | Jonathan et al.[4] (1981) | 0.56 | 0.11 | 0.33 |
| | Brandt et al.[7] (1979) | 0.24 | 0.09 | 0.67 |
| | Tamagake et al.[6] (1980) | 0.59 | 0.13 | 0.28 |
| | Aker et al.[8] (1986) | 0.63 | 0.07 | 0.30 |
| | QCT[a] | | | |
| | Beadle et al.[2] (1978) | 0.70 | 0.18 | 0.12 |
| | Jonathan et al.[4] (1981) | 0.68 | | |
| | this work | 0.63 | 0.23 | 0.14 |
| F + HI | experiments | | | |
| | Jonathan et al.[1] (1971) | 0.56 ± 0.02 | | |
| | Beadle et al.[2] (1978) | 0.57 | ≥0.07 | ≤0.36 |
| | Tamagake et al.[6] (1980) | 0.59 | 0.12 | 0.30 |
| | QCT[a] | | | |
| | Beadle et al.[2] (1978) | 0.70 | 0.12 | 0.18 |
| | this work | 0.65 | 0.23 | 0.12 |

[a] Quasiclassical trajectory calculations.

effects were determined experimentally by Würzberg et al. for all three reactions[13] and by us or the F + HBr reaction.[17,18] All these experiments show a rather small kinetic isotope effect as was also indicated by our calculations. The value calculated by us for the F + HCl reaction, 1.27, is in very good agreement with the experimental value determined by Würzberg et al., 1.38 ± 0.29.[13] The values calculated by Sayós et al. by the variational transition-state theory method, 1.70,[20] and by the quasiclassical trajectory method, 1.81 ± 0.09,[22] seem to be too high. The value calculated by us for the F + HBr reaction, 1.05, is in good agreement with our experimental value 1.07 ± 0.12[18] and is close to the lower limit of the results of Würzberg et al., 1.29 ± 0.18. The value calculated for the F + HI reaction, 1.06, is somewhat lower than the experimental value of Würzberg et al., 1.29 ± 0.14. It should be noted that very small kinetic isotope effects have been measured also for some other hydrogen-atom abstraction reactions by fluorine atoms. A value of 1.1 ± 0.2 was determined for the F + $NH_3$ reaction,[30] and a value of 1.04 ± 0.02 was determined for the F + $H_2S$ reaction.[27]

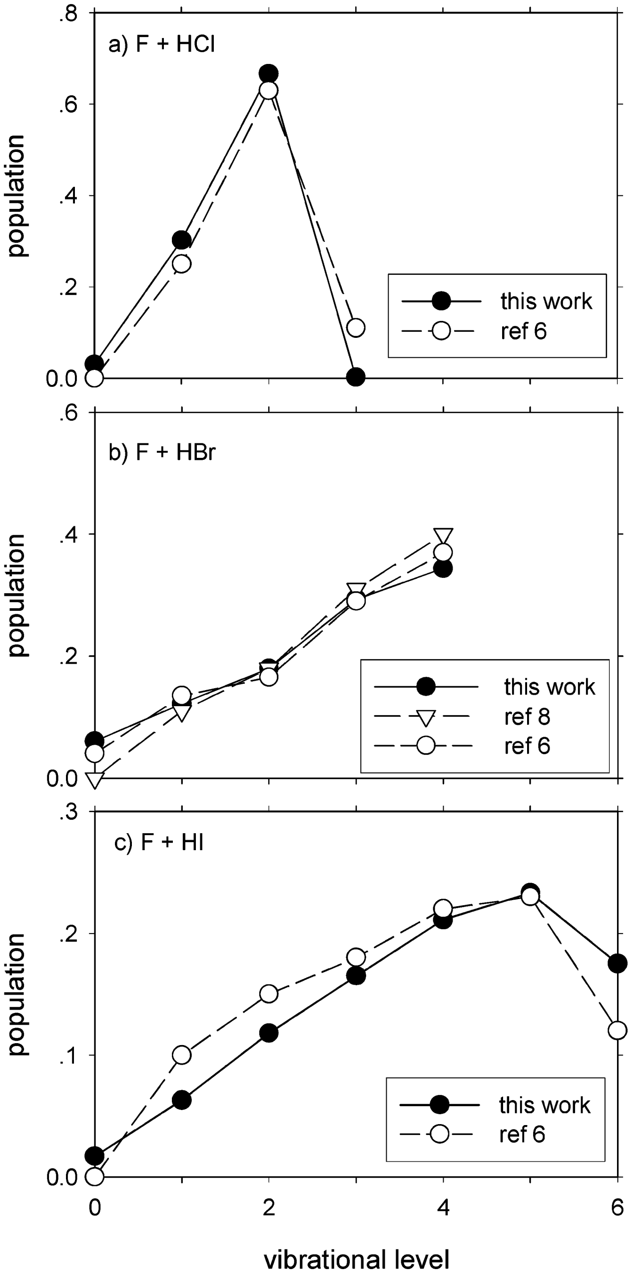

**Figure 3.** Calculated and experimental vibrational-state distributions of the product HF for the F + HX reactions. (a) F + HCl; (b) F + HBr; (c) F + HI. (●) this work; (○) experimental results from ref 6; (▽) experimental results from ref 8 for the F + HBr reaction.

**2.3. Energy Distribution among Reaction Products.** The partition of the available energy of the product HF between vibration, rotation, and translation ($f_V$, $f_R$, and $f_T$, respectively), which was obtained from our calculations, is presented in Table 4. Also presented in this table are available experimental results, as well as results of QCT calculations of other research groups.

As can be seen from Table 4, a quite good agreement between our calculations and the experiment was obtained for the F + HCl reaction, though $f_R$ is somewhat higher and $f_T$ is somewhat lower than the experimental values. Our results are comparable to the QCT results of Ding et al.[3] and are in better agreement with the experiment than those of Beadle et al.[2] and of Sayós et al.[22] Our results for the F + HBr reaction show a good agreement with the experiment for $f_V$, a somewhat too high value for $f_R$, and a too low value for $f_T$. The agreement is better than for the QCT results of Beadle et al.[2] and of Jonathan et al.[4]

**TABLE 5: Vibrational State Distributions of the HF in the Reactions F + HCl, F + HBr, and F + HI at 298 K[a]**

| reaction | investigators | $v_0$ | $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $v_6$ |
|---|---|---|---|---|---|---|---|---|
| F + HCl | Jonathan et al.[1] (1971)[b] | 0.06 | 0.27 | 0.56 | 0.10 | | | |
| | Beadle et al.[2] (1978)[c] | 0.09 | 0.26 | 0.52 | 0.13 | | | |
| | Ding et al.[3] (1973) | | 0.27 | 0.57 | 0.16 | | | |
| | Sung and Setser[5] (1977) | | 0.33 | 0.59 | 0.08 | | | |
| | Tamagake et al.[6] (1980) [d] | | 0.25 | 0.63 | 0.11 | | | |
| | Tamagake et al.[6] (1980)[e] | | 0.25 | 0.64 | 0.11 | | | |
| | Tamagake et al.[6] (1980)[f] | 0.07 | 0.23 | 0.60 | 0.10 | | | |
| | Sayós et al.[22] (2000) [g] | | 0.11 | 0.75 | 0.14 | | | |
| | this work[g] | 0.03 | 0.30 | 0.66 | 0.01 | | | |
| F + HBr | Jonathan et al.[1] (1971)[b] | 0.05 | 0.17 | 0.29 | 0.27 | 0.22 | | |
| | Beadle et al.[2] (1978)[c] | 0.06 | 0.15 | 0.18 | 0.29 | 0.32 | | |
| | Brandt et al.[7] (1979) | 0.55 | 0.21 | 0.13 | 0.06 | 0.04 | | |
| | Sung and Setser[5] (1977) | | 0.13 | 0.25 | 0.33 | 0.29 | | |
| | Tamagake et al.[6] (1980)[d] | | 0.09 | 0.22 | 0.34 | 0.35 | | |
| | Tamagake et al.[6] (1980)[e] | | 0.14 | 0.17 | 0.30 | 0.39 | | |
| | Tamagake et al.[6] (1980)[f] | 0.04 | 0.135 | 0.165 | 0.29 | 0.37 | | |
| | Aker et al.[8] (1986) | | 0.11 | 0.18 | 0.31 | 0.40 | | |
| | this work[g] | 0.06 | 0.12 | 0.18 | 0.29 | 0.35 | | |
| F + HI | Jonathan et al.[1] (1971)[b] | 0.07 | 0.09 | 0.11 | 0.13 | 0.17 | 0.25 | 0.18 |
| | Beadle et al.[2] (1978)[c] | 0.07 | 0.10 | 0.11 | 0.13 | 0.18 | 0.23 | 0.18 |
| | Sung and Setser[5] (1977) | | 0.14 | 0.16 | 0.19 | 0.20 | 0.20 | 0.11 |
| | Tamagake et al.[6] (1980) [d] | | 0.10 | 0.15 | 0.18 | 0.22 | 0.23 | 0.12 |
| | Tamagake et al.[6] (1980)[e] | | 0.11 | 0.12 | 0.14 | 0.17 | 0.21 | 0.25 |
| | Tamagake et al.[6] (1980) [f] | 0.06 | 0.10 | 0.11 | 0.13 | 0.16 | 0.20 | 0.24 |
| | this work[g] | 0.02 | 0.06 | 0.12 | 0.17 | 0.21 | 0.23 | 0.19 |

[a] All the results in this table, except for the QCT results of the present study and of ref 22, are experimental results. [b] Corrected values calculated from Table 2 of ref 2. [c] Calculated from Table 2 of ref 2. [d] Fast-flow experiments. [e] Arrested relaxation experiments. [f] The distribution, including the estimate for a $v = 0$ contribution, was made from the extrapolation of vibrational surprisal plots to $f_v = 0$. [g] Quasiclassical trajectory calculations.

Our calculations for F + HI show a slightly too high value for $f_V$, a too high value for $f_R$, and a too low value for $f_T$. The QCT results of Beadle et al.[2] show a still higher value than experiment for $f_V$ and a too low value for $f_T$.

In general, it can be concluded that our results for the three reactions are in satisfactory agreement with experiment, especially with respect to $f_V$, though the values for $f_R$ are somewhat too high and the values for $f_T$ are somewhat too low. Our results are in better agreement with experiment than those of Beadle et al.[2] who also employed LEPS potential-energy surfaces. As mentioned in section 2.2, the potential energy surfaces employed by Beadle et al. were fitted to the experimental energy distribution of the products. As shown in Table 2, the rate constants calculated by them, using these surfaces, are lower than the experimental values by 1−2 orders of magnitude. Our results for F + HCl are in better agreement with experiment than those of Sayós et al.[22] who used an ab initio potential-energy surface, which was scaled so as to fit the experimental rate constant.

The vibrational-state distributions of the product HF in the reactions F + HCl, F + HBr, and F + HI at 298 K, which were obtained from our QCT calculations, are presented in Table 5 where they are compared with available experimental data. A comparison between our results and the experimental results of Tamagake et al.[6] is shown in Figure 3. Also included in this figure are the results of Aker et al. for F + HBr.[8] As can be seen from Table 5 and Figure 3, the agreement between our calculations and the experiment is quite good for all three reactions. QCT calculations of the vibrational-state distribution on LEPS potential-energy surfaces for all three reactions were also performed by Beadle et al.,[2] but no numerical values have been reported by them. A comparison between their calculated results and their experimental results is shown in Figure 1 of their publication. This figure indicates a far less satisfactory agreement with experiment then that achieved in the present calculations. QCT calculations of the vibrational-state distribution for the F + HCl reaction on an ab initio potential-energy surface was carried out by Sayós et al.[22] They presented their results in Figure 9 of their paper. Approximate values were estimated by us from this figure, and they are included in Table 5. As can be seen from this table, our calculations agree better with the experiment than those of Sayós et al.

## 3. Summary and Conclusions

Quasiclassical trajectory calculations on LEPS potential-energy surfaces were carried out for the reactions F + HCl, F + HBr, and F + HI. The potential-energy surfaces were selected out of many surfaces that were tested systematically so as to reproduce the available experimental data concerning the rate constants and the energy distributions among products as well as possible. In general, good agreement was obtained between the calculated results and experimental data.

Calculated rate constants at 298 K are in good agreement with experiment. A linear Arrhenius temperature dependence with a small slope, corresponding to a low activation energy, was obtained for each of the three reactions. This behavior is in agreement with all the available experimental results for the range of temperatures below room temperature, except for the results of Würzberg and Houston for F + HBr.[14] The results of Würzberg and Houston indicate a very unusual behavior, especially for the F + HBr reaction. For F + HCl and F + HI, they found a slight increase (for F + HCl) or no increase (for F + HI) of the rate constant when the temperature was raised from low temperature (194 K) to room temperature and then an appreciable increase when the temperature was increased further. For F + HBr, a minimum value was obtained for the rate constant around 271 K and it increased with either raising or lowering the temperature. This behavior is in contrast to the normal behavior found in our laboratory for this reaction, as well as for the isotopomeric reaction F + DBr and for the similar reaction Cl + HBr. We believe that this unusual behavior is wrong and is due to some experimental difficulties. The small activation energies obtained from our calculations for F + HCl and F +HI are in good agreement with available experimental data. The value calculated for F + HBr (0.16 kcal/mol) is smaller than the experimental value from our laboratory (0.90 kcal/mol), though both of them indicate a slow increase of the rate with temperature.

Calculations were also carried out for the isotopomeric reactions F + DCl, F + DBr, and F + DI at 298 K. Low kinetic isotope effects were obtained in satisfactory agreement with available experimental data.

The partitioning of available energy of the product HF between vibration ($f_V$), rotation ($f_R$), and translation ($f_T$), for all three reactions, was found to be in good agreement with experiment, especially with respect to $f_V$. $f_R$ was found to be somewhat too high and $f_T$ somewhat too low. The calculated distribution of vibrational states, for each of the three reactions, was found to be in good agreement with experimental data.

The results of our calculations were compared with the results of calculations from other research groups, and we found that our results are in better agreement with experiment than the other results. Beadle et al.[2] carried out QCT calculations on LEPS potential-energy surfaces for all three reactions. Although these surfaces were chosen to obtain the best fit to the experimental vibrational-state distributions, without considering any other experimental data, their calculated distributions are in less-satisfactory agreement with experiment than our distributions. The energy partitioning between vibration, rotation, and translation is also in somewhat less satisfactory agreement with experiment than our results. The rate constants calculated by them are lower than the experimental values by 1−2 orders of magnitude, and it is therefore obvious that the potential-energy surfaces chosen by them are not suitable for any of the three F + HX reactions.

Sayós and co-workers carried out calculations only for the F + HCl reaction, employing an ab initio potential-energy surface.[20,22] This surface was scaled so that the rate constant at 300 K, calculated by the variational transition-state theory, will agree with experimental results. They also used this surface for QCT calculations, and a good agreement with the experimental rate constant was obtained. A somewhat higher value was obtained by another group, which used this surface for time-dependent quantum wave packet calculations.[21] Sayós et al. calculated also the kinetic isotope effect by the two methods used by them. In both cases, a too high value was obtained. By use of the QCT method, they also calculated the energy partitioning and the vibrational-state distribution in the product HF. Their results are in less-satisfactory agreement with experiment than our results.

We believe that this publication summarizes the available theoretical and experimental data concerning the kinetics and the energy partitioning for the F + HCl, F + HBr, and F +HI reactions. In general, the results obtained in the present study are in good agreement with experiment. The agreement is better than for the other calculations carried out until now. It seems to us that such agreement is nearly the best that can be achieved using LEPS potential-energy surfaces. More accurate potential-energy surfaces are needed in order to improve the agreement still further. Additional kinetic experiments, especially studies concerning the temperature dependence of rate constants, would also be very helpful for a thorough study of the dynamics of these reactions.

## References and Notes

(1) Jonathan, N.; Melliar-Smith, C. M.; Okuda, S.; Slater, D. H.; Timlin, D. *Mol. Phys.* **1971**, *22*, 561.
(2) Beadle, P.; Dunn, M. R.; Jonathan, N. B. H.; Liddy, J. P.; Naylor, J. C. *J. Chem. Soc., Faraday II* **1978**, *74*, 2170.
(3) Ding, A. M. G.; Kirsch, L. J.; Perry, D. S.; Polanyi, J. C.; Schreiber, J. L. *Faraday Discuss. Chem. Soc.* **1973**, *55*, 252.
(4) Jonathan, N. B. H.; Sellers, P. A.; Stace, A. *J. Mol. Phys.* **1981**, *43*, 215.
(5) Sung, J. P.; Setser, D. W. *Chem. Phys. Lett.* **1977**, *48*, 413.
(6) Tamagake, K.; Setser, D. W.; Sung, J. P. *J. Chem. Phys.* **1980**, *73*, 2203.
(7) Brandt, D.; Dickson, L. W.; Kwan, L. N. Y.; Polanyi, J. C. *Chem. Phys.* **1979**, *39*, 189.
(8) Aker, P. M.; Donaldson, D. J.; Sloan, J. J. *J. Phys. Chem.* **1986**, *90*, 3110.
(9) Kompa, K. L.; Wanner, J. *Chem. Phys. Lett.* **1972**, *12*, 560.
(10) Pollock, T. L.; Jones, W. E. *Can. J. Chem.* **1973**, *51*, 2041.
(11) Wagner, H. G.; Warnatz, J.; Zetch, C. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 571.
(12) Clyne, M. A. A.; Nip, W. S. *Int. J. Chem. Kinet.* **1978**, *10*, 367.
(13) Würzberg, E.; Grimley, A. J.; Houston, P. L. *Chem. Phys. Lett.* **1978**, *57*, 373.
(14) Würzberg, E.; Houston, P. L. *J. Chem. Phys.* **1980**, *72*, 5915.
(15) Smith, I. W. M.; Wrigley, D. *J. Chem. Phys.* **1981**, *63*, 321.
(16) Moore, C. M.; Smith, I. W. M.; Stewart, D. W. A. *Int. J. Chem. Kinet.* **1994**, *26*, 813.
(17) Edrei, R.; Persky, A. *Chem. Phys. Lett.* **1989**, *157*, 265.
(18) Schwartz, E.; Persky, A. *Chem. Phys. Lett.* **1992**, *196*, 133.
(19) Rubin, R.; Persky, A. *J. Chem. Phys.* **1983**, *79*, 4310.
(20) Sayós, R.; Hernando, J.; Hijazo, J.; González, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 947.
(21) Tang, B. Y.; Yang, B. H.; Han, K. L.; Zhang, R. Q.; Zhang, J. Z. H. *J. Chem. Phys.* **2000**, *113*, 10105.
(22) Sayós, R.; Hernando, J.; Francia, R.; González, M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 523.
(23) (a) Polanyi, J. C. *J. Quant. Spectrosc. Radiat. Transfer* **1963**, *3*, 471. (b) Persky, A.; Klein, F. S. *J. Chem. Phys.* **1966**, *44*, 3617.
(24) Aoiz, F. J.; Bañares, L.; Herrero, V. J.; Sáez Rábanos, V. *Chem. Phys.* **1994**, 187, 227.
(25) Herzberg, G. Molecular Spectra and Molecular Structure I. *Spectra of Diatomic Molecules*; Van Nostrand: New York, 1972.
(26) Persky, A. *J. Phys. Chem.* **1996**, *100*, 689. An updated value for $k_{F+CH_4}$, based on an updated recommended value for $k_{F+H_2}$, is given in ref 27.
(27) Persky, A. *Chem. Phys. Lett.* **1998**, *298*, 390. Erratum. Persky, A. *Chem. Phys. Lett.* **1999**, *306*, 416.
(28) Persky, A.; Kornweitz, H. *Int. J. Chem. Kinet.* **1997**, *29*, 67.
(29) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **2000**, *29*, 167.
(30) Manocha, A. S.; Setser, D. W.; Wickramaaratchi, M. A. *Chem. Phys.* **1983**, *76*, 129.