Spin–orbit branching in the photodissociation of HF and DF. II. A time-dependent wave packet study of vibrationally mediated photodissociation

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The vibrationally mediated photodissociation dynamics of HF and DF, following $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ electronic excitation, are examined using time-dependent wave packet techniques. Predictions of the branching fraction for the formation of excited state fluorine, $F(^2P_{1/2})$, are made for a wide range of excitation energies and for the initial vibrational states $v = 1, 2,$ and 3. The preceding article (Ref. 33) discusses the underlying theory and presents results for photodissociation from the ground vibrational state ($v=0$). The calculated branching fraction for HF photodissociation from the $v = 3$ vibrational state agrees well with the value of 0.42 ± 0.03 measured experimentally at 193.3 nm by Zhang et al. [J. Chem. Phys. **104**, 7027 (1996)]. The results are discussed in context with the corresponding results for HCl and DCl. © *2000 American Institute of Physics.* [S0021-9606(00)01629-9]

I. INTRODUCTION

The photodissociation dynamics of the hydrogen halides, HX (X=F, Cl, Br, and I), have received a great deal of experimental[1–22] and theoretical[21–32] study. One reason for these extensive investigations is that the hydrogen halides are excellent model systems for photodissociation involving multiple coupled excited states. The preceding article (Ref. 33) presents the underlying theory that we use to model the photodissociation dynamics of HF. As illustrated for the case of HF in Fig. 1 of the preceding article, neglecting spin–orbit coupling, four electronic states ($X\,^1\Sigma^+$, $A\,^1\Pi$, $a\,^3\Pi$, and $1\,^3\Sigma^+$) correlate with the lowest energy asymptote, $H(^2S) + X(^2P)$. One of the most interesting aspects of the photodissociation process lies in the fact that the halogen atom can be produced in either of its spin–orbit component states, $X(^2P_{3/2})$ or $X(^2P_{1/2})$. Measurement of the relative yields of the two spin–orbit states and, in some cases, the angular distribution of the photofragments, provides information regarding the excited states involved in the initial excitation and how the photofragment flux is redistributed among the coupled excited states as the molecule fragments. In the photodissociation of HCl,[2–6,21–27] HBr,[7–13,28,29] and HI,[14–19,32] the roles of these two processes have been studied in detail but little work has been done for HF.[1,33] The body of work on HF is limited due to the experimental difficulties of studying a molecule which absorbs primarily in the vacuum ultraviolet (VUV)[34,35] and which is highly corrosive.

The relationship between the two processes, initial excitation and flux redistribution, involved in the hydrogen halide photodissociation alters as the halogen atom changes from fluorine to iodine: the spin–orbit coupling increases as the nuclear charge increases. For the low nuclear charge halogens, F and Cl, the dominant initial transition involves excitation from the ground $X\,^1\Sigma^+$ state to the repulsive $A\,^1\Pi$ state.[21,25,33] As the spin–orbit interaction increases, initial excitations which are nominally spin-forbidden increase in importance. For example, initial excitation to the $^3\Pi_{\Omega=0^+}$ state has been shown to play a minor role in HCl dissociation[25] and a more important role in HBr dissociation.[28,29] States designated with the quantum number Ω refer to the fully adiabatic (i.e., spin–orbit coupled) states, while those without this label refer to the diabatic (neglecting spin–orbit coupling) states. The fully adiabatic states are properly characterized by the Ω label only; however, as is commonly done, we retain the case (a) labeling which designates the diabatic state with the largest contribution to the fully adiabatic state in the Franck–Condon region (see preceding article for a more complete discussion).

The VUV absorption spectrum of HF is broad and featureless, indicating a prompt dissociation, and peaks at around 83 000 cm^{-1}.[34,35] The initial excitation in HF is assigned to the $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ transition.[33–36] Following the initial excitation, there can be a redistribution of flux as HF fragments to produce both fluorine spin–orbit components

$$\begin{aligned} HF + h\nu &\rightarrow H(^2S) + F(^2P_{3/2}) \\ &\rightarrow H(^2S) + F(^2P_{1/2}). \end{aligned} \quad (1)$$
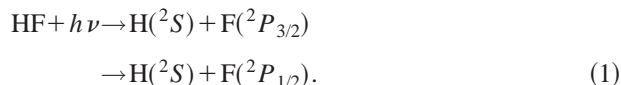
Using the customary nomenclature, the fluorine atom spin–orbit states are designated as F and F* for $F(^2P_{3/2})$ and $F(^2P_{1/2})$, respectively. The relative yield of these two products is characterized by the photon energy dependent excited state F* branching fraction

$$\Gamma(\nu) = \frac{\sigma^*}{\sigma + \sigma^*} = \frac{\sigma^*}{\sigma_{\text{total}}}, \quad (2)$$

where $\sigma \equiv \sigma(F)$ and $\sigma^* \equiv \sigma(F^*)$ are the cross-sections for the production of ground and excited state fluorine atoms at a particular photon energy.

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The full adiabatic potential energy curves which correlate with the $H(^2S)+F(^2P_J)$ asymptotes have been presented in Fig. 4 of Ref. 33. These curves are obtained by diagonalizing the energy matrix containing the diabatic potential energies plus the spin–orbit coupling between these states, see Figs. 1 and 3 of Ref. 33, respectively. It can be seen that the nominal $^1\Pi_1$ state correlates adiabatically with ground state fluorine $F(^2P_{3/2})$. Therefore, if there were no redistribution of flux following initial excitation, the excited state branching fraction would be zero. However, Wittig and co-workers[1] have measured a branching fraction of 0.41 ± 0.12 for excitation from $v=0$ and 0.42 ± 0.03 for excitation from $v=3$. These results imply that nonadiabatic transitions occur as the molecule breaks apart. Similar results for HCl have been seen experimentally[2–6,21] and explained theoretically[21,25] based on *ab initio* calculations. In the companion article,[33] the HF results following excitation from the ground ($v=0$) vibrational state are explained.

While there have been many studies of hydrogen halide photodissociation following excitation from the ground vibrational state ($v=0$), there have been fewer studies investigating the role of initial vibrational excitation on the dynamics and, most importantly, the excited state branching fraction. Measurement of the branching fraction for vibrationally mediated photodissociation (VMP) provides a sensitive probe of the potential energy surfaces and the nonadiabatic couplings connecting them. The first experiment involving VMP of the hydrogen halides was carried out by Zittel and Little,[12] who measured the absorption cross-section for HBr ($v=1$). However, they did not examine any of the detailed dynamics, i.e., the anisotropy parameter or the spin–orbit branching fraction. Subsequently, more detailed studies of the VMP of HBr were carried out experimentally[13] and theoretically.[28] There have been several calculations on the VMP of HCl,[23,24] but it is only recently that a theoretical study has been combined with experimental results measuring the branching fraction from the vibrational states $v=1$, 2, and 3.[22] While the agreement between theory and experiment was satisfactory, it was not nearly as good as the agreement that was obtained for excitation from $v=0$. Finally, theoretical predictions regarding the use of VMP for controlling the branching fraction in HI have been made by Chakrabarti and Sathyamurthy.[30] However, recent experiments[7,14] have shown that these predictions were based upon incorrect potential energy curves and nonadiabatic couplings.

For HF, Wittig and co-workers[1] measured the branching fraction following excitation at 193.3 nm from the $v=3$ vibrational state using the H-atom Rydberg time-of-flight technique. They measured the branching fraction to be 0.42 ± 0.03 as compared to 0.41 ± 0.12 following excitation at 121.6 nm from $v=0$. While these results are interesting, a more thorough investigation of the energy dependence of the branching fraction as a function of the initial vibrational level can be carried out theoretically, and we hope that this theoretical investigation will prompt renewed experimental interest.

This article reports the first theoretical study of the spin–orbit branching in the vibrationally mediated photodissociation of HF and DF and complements our results for excitation from $v=0$, reported in the preceding article. The theory used is identical to that of Ref. 33 (preceding article) and is outlined in Sec. II of that work. In Sec. II of this article, our predictions for the branching fraction are presented, as a function of wavelength, for excitation from the vibrational states $v=1$, 2, and 3. The frequency dependence of these results is discussed in terms of the initial excitation and the transfer of flux between the excited state potential energy curves. The results for HF and DF are compared and contrasted to the corresponding results in HCl and DCl. Finally, some brief conclusions are drawn in Sec. III.

II. RESULTS AND DISCUSSION

The vibrationally mediated photodissociation dynamics of HF can be studied using the previously calculated potential energy curves and spin–orbit couplings.[33] In order to confirm that the potential energy curve for the ground electronic state is sufficiently accurate, the vibrational wave functions and energies for the lowest four vibrational states, $v=0$, 1, 2, and 3, of both HF and DF have been calculated using the Fourier grid Hamiltonian method.[37] The results for HF and DF are presented in Tables I and II, respectively, along with vibrational energies which have previously been determined by fitting experimental data.[38–40] The computed vibrational energies agree well (within 1%) with the experimentally fitted results. It may be inferred from this agreement that the ab initio ground state potential energy curve provides a good representation of the true potential.

The partial cross-sections, as well as the corresponding excited state spin–orbit branching fractions, have been calculated as a function of photon energy following excitation from the vibrational states $v=1$, 2, and 3. The results for excitation from the $v=0$ vibrational state have been pre-

TABLE I. Vibrational energy levels for the $X\,^1\Sigma^+$ ground state of HF. Values are measured from the minimum of the ground state potential energy curve and are given in cm^{-1}.

Vibrational state	Present calculation[a]	Ref. 38[b]	Ref. 39[c]
0	2057.4	2046.69	2046.82
1	6034.1	6005.25	6008.25
2	9841.1	9784.05	9797.66
3	13 483.7	13 383.08	13 419.85

[a]Obtained using the Fourier grid Hamiltonian method (Ref. 37).
[b]Obtained by fitting experimental data.
[c]Obtained by simultaneously fitting the HF and DF experimental data.

TABLE II. Vibrational energy levels for the $X\,^1\Sigma^+$ ground state of DF. Values are measured from the minimum of the ground state potential energy and are given in cm^{-1}.

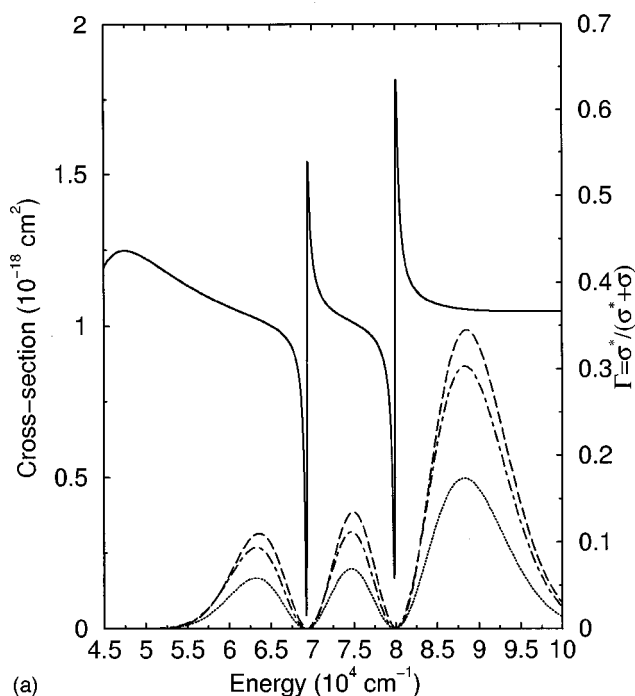| Vibrational state	Present calculation[a]	Ref. 39[b]	Ref. 40[c]
0	1493.93	1488.27	1490.30
1	4410.60	4394.93	4396.97
2	7236.55	7210.09	7212.12
3	9975.44	9935.67	9937.66

[a]Obtained using the Fourier grid Hamiltonian method (Ref. 37).
[b]Obtained by fitting experimental data.
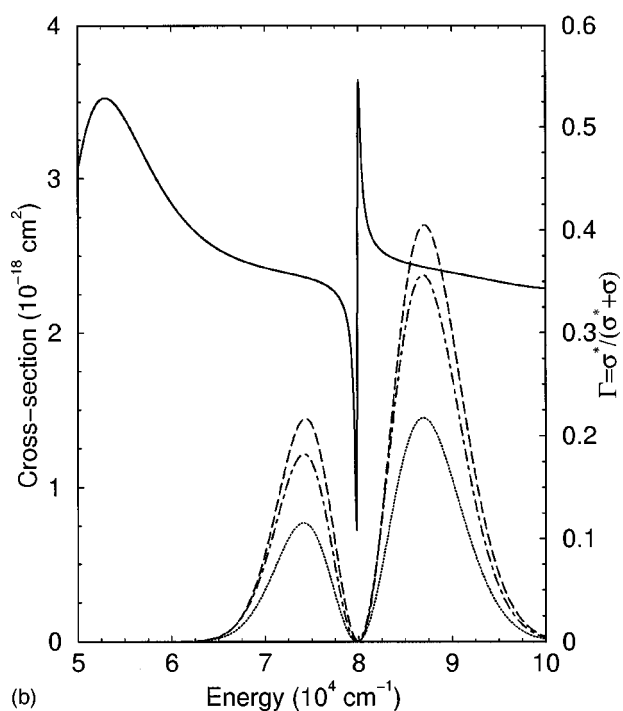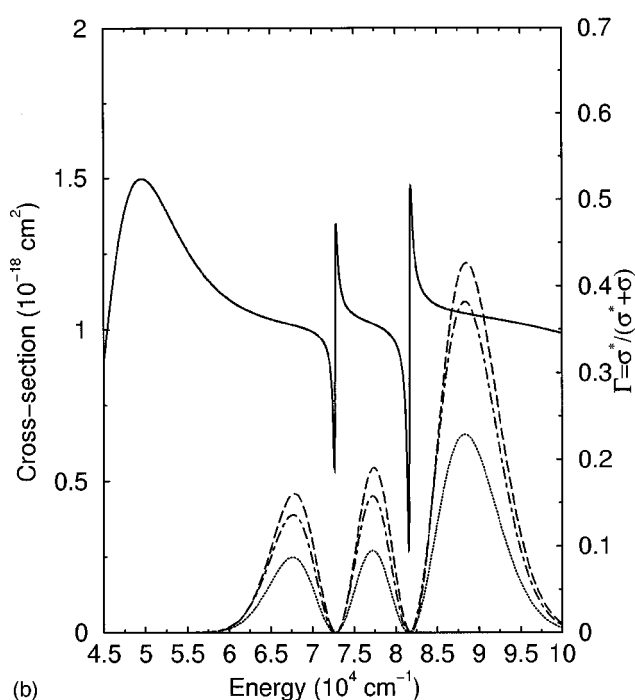[c]Obtained by simultaneously fitting the HF and DF experimental data.
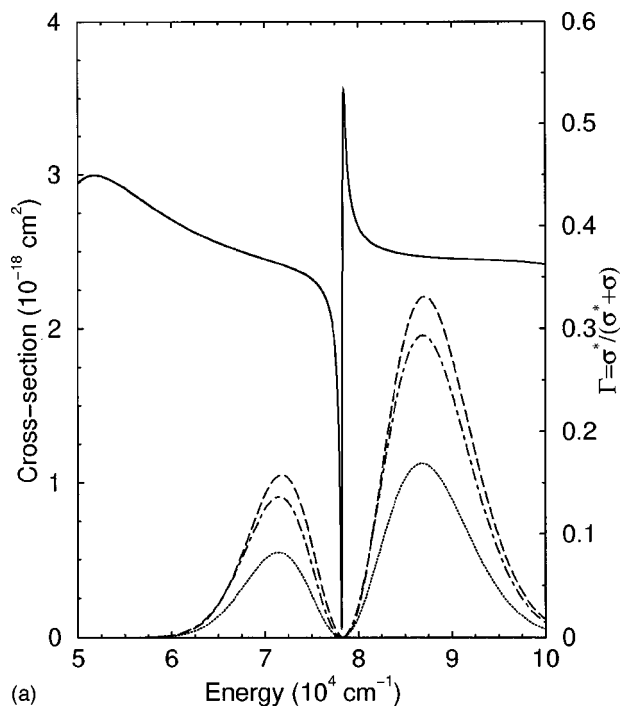
FIG. 1. The partial photodissociation cross-sections, $^3\Pi_1$ (dashed line), $^1\Pi_1$ (dotted line), and $^3\Sigma_1$ (dot-dash line), and the F atom branching fraction (solid line), $\Gamma = \sigma(F^*)/[\sigma(F^*) + \sigma(F)]$, as a function of photon energy for photodissociation out of the $v = 1$ vibrational state for (a) HF and (b) DF. The cross-sections are identified by their nominal case (a) labeling and the good quantum number Ω.

FIG. 2. The partial photodissociation cross-sections, $^3\Pi_1$ (dashed line), $^1\Pi_1$ (dotted line), and $^3\Sigma_1$ (dot-dash line), and the F atom branching fraction (solid line), $\Gamma = \sigma(F^*)/[\sigma(F^*) + \sigma(F)]$, as a function of photon energy for photodissociation out of the $v = 2$ vibrational state for (a) HF and (b) DF. The cross-sections are identified by their nominal case (a) labeling and the good quantum number Ω.

sented in the preceding paper.[33] The results for HF, $v = 1$, 2, and 3, are illustrated in Figs. 1(a), 2(a), and 3(a), respectively, while Figs. 1(b), 2(b), and 3(b) show the corresponding results for DF photodissociation. The experimentally determined branching fraction of Wittig and co-workers[1] for the photodissociation of HF ($v = 3$) at 193.3 nm is shown in Fig. 3(a). This represents the only experimental data point

for the VMP of HF or DF with which our computed results may be compared. From examining Figs. 1–3, there are clearly several features which are common to the photodissociation from any vibrational state and for both HF and DF.

The partial cross-sections all exhibit oscillatory behavior, where the number of minima is equal to the number of nodes in the ground state vibrational wave function, i.e., one
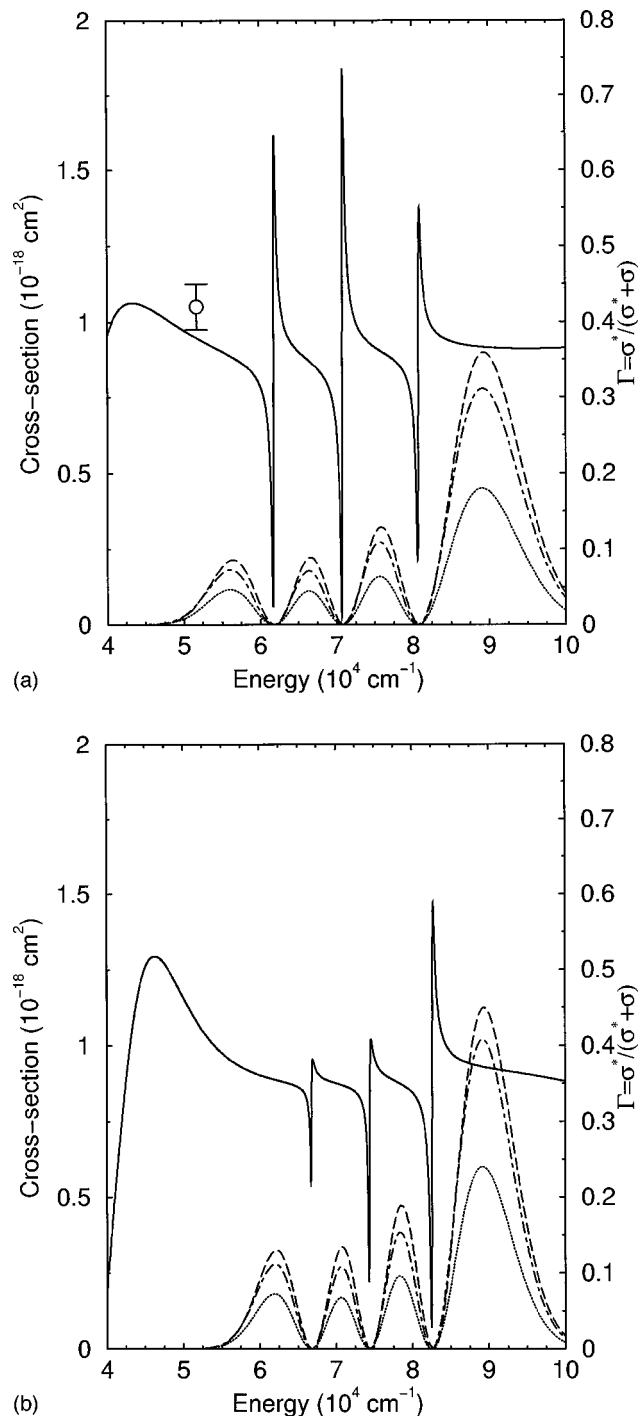
FIG. 3. The partial photodissociation cross-sections, $^3\Pi_1$ (dashed line), $^1\Pi_1$ (dotted line), and $^3\Sigma_1$ (dot-dash line), and the F atom branching fraction (solid line), $\Gamma = \sigma(F^*)/[\sigma(F^*) + \sigma(F)]$, as a function of photon energy for photodissociation out of the $v=3$ vibrational state for (a) HF and (b) DF. Also, shown is the experimentally measured branching fraction of Wittig and co-workers (Ref. 1) at 193.3 nm for HF. The cross-sections are identified by their nominal case (a) labeling and the good quantum number Ω.

for $v=1$, two for $v=2$, and three for $v=3$. While the minima in the partial cross-sections are expected, in agreement with the reflection principle,[41] it is not readily apparent why there are minima (and accompanying maxima) in the branching fractions near the frequencies where the cross-section minima appear. Nodal behavior in the branching fractions has also been calculated for the VMP of HCl[22–24]

and DCl;[42] the presence of these nodes has not been experimentally verified. Upon closer inspection, the source of the minima (and maxima) in the spin–orbit branching fractions is a slight shift in the positions of the minima in the partial cross-sections. Tables III and IV list the frequencies at which the minima of the partial cross sections occur for HF and DF, respectively. Clearly, the frequencies at which the production of F* and F reach minima do not coincide, resulting in the minima (and maxima) in the F* branching fractions near the minima of the partial cross-sections. Since two cross-sections, whose minima do not coincide, are correlated with F (i.e., $^3\Pi_1$ and $^1\Pi_1$), the exact positions and depths of the minima (maxima) in the branching fractions are due to subtle interplay between the positions and magnitudes of the cross-sections. For example, the minimum in the F* partial cross-section for HF ($v=1$) occurs for a photon energy of 78 175 cm^{-1}. This minimum is located between the minima of the two partial cross-sections corresponding to F production at 78 123 and 78 407 cm^{-1}. From these cross-sections, the minimum of the branching fraction occurs at 78 175 cm^{-1}, while the maximum occurs at 78 449 cm^{-1}. As has been shown for HCl,[23] small changes in the couplings between the diabatic states can have large effects in the observed branching fractions in the vicinity of these partial cross-section minima.

The branching fractions for HF and DF all exhibit a maximum at low energy, $<56\,000$ cm^{-1} (see Figs. 1–3). The position of the maximum shifts to lower energy as the initial vibrational state changes from $v=1$ to $v=3$. The shift in the overall position of the cross-section to lower energy with

TABLE III. Minima in the partial cross-sections for excitation from particular initial vibrational states for HF. Energies are given in cm^{-1}.

Vibrational state	State[a]	E_{min}	E_{min}	E_{min}
1	$^3\Pi_1$	78 123	⋯	⋯
	$^1\Pi_1$	78 407	⋯	⋯
	$^3\Sigma_1$	78 175	⋯	⋯
2	$^3\Pi_1$	69 203	79 881	⋯
	$^1\Pi_1$	69 466	80 102	⋯
	$^3\Sigma_1$	69 245	79 871	⋯
3	$^3\Pi_1$	61 709	70 768	80 647
	$^1\Pi_1$	61 909	70 947	80 868
	$^3\Sigma_1$	61 688	70 705	80 668

[a]Identified by nominal case (a) labeling and the good quantum number Ω.

TABLE IV. Minima in the partial cross-sections for excitation from particular initial vibrational states for DF. Energies are given in cm^{-1}.

Vibrational state	State[a]	E_{min}	E_{min}	E_{min}
1	$^3\Pi_1$	79 809	⋯	⋯
	$^1\Pi_1$	79 967	⋯	⋯
	$^3\Sigma_1$	79 799	⋯	⋯
2	$^3\Pi_1$	72 701	81 571	⋯
	$^1\Pi_1$	72 828	81 813	⋯
	$^3\Sigma_1$	72 722	81 623	⋯
3	$^3\Pi_1$	66 743	74 318	82 535
	$^1\Pi_1$	66 869	74 497	82 766
	$^3\Sigma_1$	66 795	74 381	82 535

[a]Identified by nominal case (a) labeling and the good quantum number Ω.

increasing initial vibrational state has two sources: the molecule begins with an increased initial energy and the ground state vibrational wave function has substantial amplitude at larger internuclear separations where the energy separation between the ground and excited states is smaller. In addition to shifting to lower energy, the height of the branching fraction maximum, Γ_{max}, decreases with increasing initial vibrational state. For HF, Γ_{max} goes from 0.449 to 0.437 to 0.425 as the vibrational state changes from $v=1$ to 2 to 3. Similarly for DF, the maximum branching fraction, which is always greater than its HF counterpart, changes from 0.529 to 0.524 to 0.518 for the corresponding change in initial vibrational state. While this decrease is interesting to note, a change of this magnitude would be very difficult to detect experimentally.

The low-energy maximum in the branching fraction is also seen following excitation from $v=0$ for HF and DF.[33] For HCl, a similar low-energy maximum is calculated following excitation from $v=0$[25] and from $v=1$, 2, and 3.[22] However, for DCl, no low-energy maximum is seen for any initial vibrational state.[25,42] Examining Figs. 1–3, for both HF and DF, a maximum in the excited state branching fraction accompanies each minimum in the branching fraction (in the vicinity of the minima in the partial cross-sections). Similar behavior is exhibited in the VMP of HCl,[22–24] but not for the VMP of DCl.[42] The excited state branching fractions for DCl, while exhibiting nodes in the vicinity of minima in the partial cross-sections, have no maxima. In summary, the appearance of maxima in the excited state branching fraction for HF, DF, and HCl appears to be a general phenomenon near nodes in the partial cross-sections. The low-energy maxima appear in the region where the absorption begins, or, in other words, in the vicinity of the low-energy threshold of the absorption line.

Our calculated branching fraction for HF ($v=3$) photodissociation at 82 237 cm^{-1} (121.6 nm) of 0.37 agrees well with the experimentally measured result, 0.41 ± 0.03, of Wittig and co-workers.[1] From this excellent agreement, we conclude that the results computed over the large energy range for all vibrational states are a reliable representation of the partial photofragmentation cross-sections and of the branching fractions.

III. CONCLUSIONS

The time-dependent wave packet technique has been used to compute the partial cross-sections and accompanying excited state branching fractions for the vibrationally mediated photodissociation (VMP) of HF and DF. The partial cross-sections all exhibit nodes due to the well-known reflection principle.[41] The nodes in the cross-sections are accompanied by nodes in the branching fractions due to slight differences in the positions of the minima of the partial cross-sections for the different product atomic energy levels.

It is interesting that a minimum in the branching fraction always has an accompanying maximum for both HF and DF, including the minimum which corresponds to the onset of absorption. However, while HCl exhibits this behavior, no maxima are seen in the branching fractions for DCl. In comparing HF and HCl, two systems, which are electronically

very similar, exhibit comparable behavior in their subsequent photodissociation, i.e., the branching fractions as functions of photon energy and initial vibrational state are similar. Of more importance, the results which compare DF to HF and DCl to HCl show that small mass-effects can have very large effects on the subsequent dynamics. So while HF and HCl are electronically similar and the relative reduced masses of DF/HF ($m_{DF}/m_{HF}=1.9032$) and DCl/HCl ($m_{DCl}/m_{HCl}=1.9445$) are only different by 2%, these subtle changes show up in large ways in the calculated results. It should be possible to verify the HF and DF results experimentally; experimental results comparing HCl[2,21,25] and DCl[5,20] have recently become available.

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