Influence of Vibrational Excitation on the Reaction of $F^-$ with CH$_3$I: Spectator Mode Behavior, Enhancement, and Suppression

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ABSTRACT: Detailed insight into chemical reaction dynamics can be obtained by probing the effect of mode-specific vibrational excitation. Suppression or enhancement of reactivity is possible as is already known from the Polanyi rules. In the reaction $F^- + CH_3I$, we found vibrational enhancement, suppression, and spectator mode dynamics in the four different reaction channels. For this system we have probed the influence of symmetric CH-stretching vibration over a collision energy range of 0.7–2.3 eV. Proton transfer is significantly enhanced, while for the nucleophilic substitution channel the spectator mode dynamics at lower collision energies unexpectedly move toward enhancement at higher collision energies. In contrast, for two halide abstraction channels, forming FI$^-$ and FHI$^-$, we found an overall suppression, which stems mainly from a suppression of the FHI$^-$ product. We compare these results to quasiclassical trajectory calculations and with the sudden vector projection model.

A central goal of physical chemistry is to describe chemical reactions on a fundamental level. Such descriptions include atomic-level mechanisms, the collision energy dependence of the reactivity, and the energy partitioning among different reaction products. Key questions are how individual quantum states influence both reaction rates and dynamics, especially in comparison with equal amounts of kinetic or thermal energy, meaning statistically distributed energy in all internal degrees of freedom. A vibrational mode can either be a spectator for a reaction, i.e., not affect the reaction at all, or influence it by enhancing or suppressing it. To predict the influence of vibrational versus translational energy, the well-known Polanyi rules were developed for atom diatom A + BC reactions based on the position of the transition state along the reaction coordinate. In the last years the sudden vector projection (SVP) model has extended this concept to gas-phase reactions of polyatomic molecules and to reactions at surfaces. Within the SVP model one uses the overlap of each individual rovibrational mode and the translation vector with the reaction coordinate at the transition state to quantify the effective coupling. To unravel the influence of individual modes on reaction dynamics quasi-classical trajectory (QCT) calculations are the state-of-the-art method.

A powerful tool to obtain experimental insight into fundamental aspects of chemical reactions are differential cross sections. These can be measured in crossed beam experiments under single-collision conditions, for instance with the velocity map imaging technique. With the development of suitable lasers for state preparation, such experiments are able to track state-dependent differences in the reaction dynamics as well as overall reactivity. A main focus has been on the well-studied F + H$_2$ reaction as well as on reactions of halides with partially deuterated methane and water. In the case of atomic O and F reacting with CHD$_3$, the observed enhancement and suppression due to C–H stretching vibration could be assigned in comparison with high-level QCT calculations to steric effects. These effects are caused by a change in the long-range interaction, due to a change in the dipole moment caused by the vibration, that steers the approaching reactants into or away from the favored geometry.

Reactions of halide anions with methyl halides represent the simplest gas-phase bimolecular nucleophilic substitution $S_N2$ systems and are therefore ideally suited to probe their atomistic reaction mechanisms. In close cooperation with QCT calculations, we could identify the underlying reaction mechanisms and gained insight into how various aspects such as microsolvation or properties of the nucleophile and leaving group influence the reaction dynamics. One of the systems of interest is the reaction of $F^- + CH_3I$. QCT calculations have shown that a preferred approach along one of the C–H bonds leads to complex-mediated “indirect” dynamics at low collision energies in the $S_N2$ channel and large proton-transfer (PT) branching ratios, which we could confirm experimentally. The $S_N2$ channel is dominant in the investigated collision...
energy range, but the proton transfer quickly rises to approximately 20% of the total flux above the appearance threshold.25 At sufficiently high collision energy two halide abstraction (HA) pathways open up, one of which, the formation of FHI−, was observed by our group for the first time.25 Recently, we have started to study the influence of symmetric CH-stretching vibration on the S_N2 channel and can confirm the proposed spectator mode behavior.26

The four reaction pathways for the reaction of F− + CH₃I and their calculated reaction enthalpies are

\[ \text{F}^- + \text{CH}_3\text{I} \rightarrow \text{I}^- + \text{CH}_2\text{F} \quad \Delta H = -1.96 \text{ eV} \quad (\text{S}_N2) \quad (1) \]

\[ \text{F}^- + \text{CH}_3\text{I} \rightarrow \text{CH}_2\text{I}^- + \text{HF} \quad \Delta H = 0.69 \text{ eV} \quad (\text{PT}) \quad (2) \]

\[ \text{F}^- + \text{CH}_3\text{I} \rightarrow \text{F}^- + \text{CH}_3 \quad \Delta H = 0.7 \text{ eV} \quad (\text{HA}) \quad (3) \]

\[ \text{F}^- + \text{CH}_3\text{I} \rightarrow \text{FHI}^- + \text{CH}_2 \quad \Delta H = 0.9 \text{ eV} \quad (\text{HA}) \quad (4) \]

The enthalpies are taken from ref 4 for reactions 1 and 2 and ref 25 for reactions 3 and 4. An important question is if and to what extent vibrational excitation acts differently on the different pathways. With regard to reactions 3 and 4, it is also interesting to find out whether they occur via a similar attack of F− to one of the hydrogen atoms as in reactions 1 and 2 or via a frontside attack on the iodine side.

In this study we compare the influence of the CH-stretching excitation on the four different reaction channels that occur in F− + CH₃I reactions. Using an improved experimental procedure compared to our previous work,26 we could study three different relative collision energies: The lowest collision energy of 0.7 eV was chosen, because the proton-transfer channel just opens up leading to large observable enhancement. To compare translational and vibrational energy, we selected 1.2 eV, as it is close to the sum of the lowest collision energy and one vibrational quantum in the CH-stretching mode. Finally, we studied 2.3 eV collision energy, where not only the aforementioned channels but also the two halide abstraction channels are accessible.25 Very different response to vibrational excitation is found for the different reaction channels. For the S_N2 and the proton-transfer channels we compare our results in the following with theoretical predictions from recent QCT and SVP calculations by the Czako5 and Guo groups.26

The experiment has been performed using the ion–molecule crossed-beam imaging spectrometer that we have developed in recent years.27 With 20 Hz repetition rate, packets of F− anions are crossed with a supersonic jet of CH₃I seeded in helium. For every other crossing of the reactants, an infrared excitation laser drives a few percent population into the first excited level of the CH-stretching vibration of CH₃I. A detailed description of the experiment is presented in the Supporting Information. On average, less than one product ion is created per bunch crossing. For all product ions the arrival time is recorded with a photomultiplier tube attached to the velocity map imaging spectrometer. Correlated to the arrival time information, the imaging spectrometer yields the two ion velocity components parallel to the detector surface. From these data, product ion mass spectra and three-dimensional differential scattering images for each product mass are derived.

The change in reactivity due to the excited CH-stretching vibration is determined by integration of the product time-of-flight distributions (shown in Figure 1) recorded alternatingly with and without the infrared excitation laser present. The integrated number of single-ion counts for each product mass at the different collision energies are listed in the third and fourth column of Table 1. Table 1 also shows the absolute differences and relative changes with their respective uncertainty obtained from counting statistics. The relative change is illustrated in bar graphs in Figure 2 for each collision energy and reaction pathway. The fraction of CH₃I molecules in the target beam that is vibrationally excited has been monitored using a resonance-enhanced multiphoton ionization scheme26 (see the Supporting Information for details). We have measured vibrationally excited CH₃I fractions of 4.5 ± 0.5, 2.7 ± 0.4, and 2.9 ± 0.3% for the data sets taken at 0.7, 1.2, and 2.3 eV collision energy, respectively. Using these fractions, the relative change in reactivity is scaled up for each channel and collision energy. The results are shown in the last column of Table 1.

The proton-transfer channel is enhanced over the whole collision energy range, and the enhancement is strongest close to the appearance energy as can be seen from the bar graphs in Figure 2. The overlap of the blue and red bars indicates no change in reactivity. The CH-stretching vibration of CH₃I is important in the proton-transfer channel.28 It was previously suggested that the CH-stretching vibration will break the symmetry present in the reaction potential energy surface and will therefore enhance the proton-transfer channel.28 Other interpretations include that the change in reactivity due to the CH-stretching vibration is caused by collisions with the CH⁻ bond not breaking immediately but being broken by a subsequent collision.29 It is also possible that the change in reactivity is caused by an increase in charge separation during the reaction.30

Figure 1. Time-of-flight distributions for reactions with ground-state CH₃I at 0.7, 1.2, and 2.3 eV collision energy. The overlapping products FI− and FHI− are magnified in the inset in the third panel. A fitted sum of two Gaussians that is used to determine the individual contributions is drawn in the inset.
Table 1. Ion Counts for Each Product Channel with the Calculated Difference and Scaled Change Due to Vibrational Excitation

| Product channel | Collision energy | IR off (counts) | IR on (counts) | Difference | Change in % | Change in % (scaled) |
|-----------------|------------------|----------------|---------------|------------|-------------|---------------------|
| I−              | 0.7 eV           | 523 317        | 523 212       | −105 ± 1023| −0.02 ± 0.20| −0.5 ± 4.5          |
|                 | 1.2 eV           | 484 103        | 483 596       | −807 ± 984 | −0.17 ± 0.20| −6.3 ± 7.4          |
|                 | 2.3 eV           | 358 461        | 360 689       | +2 228 ± 848 | +0.62 ± 0.24| +21.4 ± 8.5         |
| CH2I            | 0.7 eV           | 5 673          | 7 156         | +1 483 ± 113| +26 ± 2     | +580 ± 75           |
|                 | 1.2 eV           | 78 713         | 83 224        | +4 511 ± 402| +5.7 ± 0.5  | +211 ± 35           |
|                 | 2.3 eV           | 88 551         | 89 907        | +1 356 ± 422| +1.5 ± 0.5  | +53 ± 17            |
| F− + FHI        | 2.3 eV           | 50 896         | 50 414        | −482 ± 318 | −1 ± 0.6    | −33 ± 22            |
| CH2I            | 2.3 eV           | 35 012         | 34 616        | −397 ± 357 | −1.1 ± 1.0  | −39 ± 35            |
| FHI−            | 2.3 eV           | 29 330         | 28 741        | −589 ± 342 | −2.0 ± 1.1  | −69 ± 40            |

“O"The scaled values are calculated from the measured excited fractions. Vibrationaly excited CH2I fractions of 4.5 ± 0.5, 2.7 ± 0.4, and 2.9 ± 0.3% for the data sets taken at 0.7, 1.2, and 2.3 eV collision energy were achieved. “O"The values for the individual dihalide channels were obtained from a Gaussian fit to the product ion mass spectra.

Figure 2b. These data have already been discussed in a recent publication and are presented here for comparison with the other three reaction channels. In contrast, we observe almost no change for the SN2 channel at the lower collision energies. At 0.7 eV, which coincides with the opening of the proton transfer, we observe a change of 105 counts or a scaled change of −0.5 ± 4.5% (see Table 1). In terms of accuracy, this is a major improvement over our previous result of 21% in promoting this reaction dynamics, in contrast to what we found for proton transfer. It is instructive to compare the experimental changes with the SVP values calculated by Guo and co-workers for both the SN2 and proton-transfer channels. The overlaps for the proton-transfer reaction coordinate give a value for the symmetric CH-stretching vibration of 0.33 compared to 0.02 for translation. This enhancement is in qualitative agreement with the experimental results shown in Figure 2. It also fits our observation that vibration is more efficient at promoting this pathway compared to translation, at least above 1 eV collision energy. For the SN2 channel they find values of 0.03 and 0.16 for the symmetric CH-stretching vibration and translation, which is in agreement with spectator mode behavior. Interestingly, the SVP method is based on the assumption of direct dynamics, i.e., a sudden reaction upon impact of the reactants, which does not apply to the majority of the reactions at 0.7 eV collision energy. Only at higher collision energies do the reactions occur predominantly by direct mechanisms (see Table S1), which means the prediction should work best at 2.3 eV. It was therefore unexpected at this collision energy to find an enhancement for the nucleophilic substitution and not clear spectator mode behavior.

We also compare our results to recent QCT calculations by the Czakó group, which cover a number of vibrational modes over a collision energy range up to 1.5 eV. The calculations find a slight suppression of the SN2 channel below 0.5 eV of about −10% and a trend toward enhancement at higher collision energies amounting to approx +7% at 1.5 eV. At 0.7 eV the change due to symmetric CH-stretching vibration is +6% and +7% at 1.2 eV. This is in quantitative agreement with the scaled experimental values (see Table 1). The observed enhancement at 2.3 eV also fits the general trend found in the calculations. For the proton transfer the QCT results find different enhancement factors, depending on the applied zero-point energy (ZPE) constraints, of 4.2 and 870 at 0.7 eV for no and soft ZPE constraints. At 1.2 eV collision energy they find factors of 2.3 and 4.7 without and with soft constraints. This is in reasonable agreement with the experimental values of 6.9 ± 0.8 and 3.0 ± 0.4, respectively. The enhancement factor at 2.3 eV has not been calculated.
respectively, the statistical accuracy of the determined changes under vibrational excitation are limited. Nevertheless, we clearly find an overall suppression for the sum of both channels. As the change in the F⁺ product alone is barely significant, we expect that the overall suppression is dominated by the FHI⁻ channel. Within the error budget, the scaled change of ~69 ± 40% is even compatible with a complete closing of this reaction channel.

For the FHI⁻ channel, the product ion velocity distributions provide additional information. Figure 3 shows the velocity distribution in the center-of-mass frame for ground state (Figure 3a) and for the difference with and without IR laser present (Figure 3b), leading to FHI⁻ along with the derived internal energy and angular distributions. To obtain these, only the right half of the time-of-flight distribution was used to minimize the influence of FI⁻ products. The black and red circles indicate the maximum velocity if all available energy is transferred into kinetic energy. The ground-state reaction shows dominant direct, forward scattering with a small indirect contribution around zero velocity. For the difference image, we find negative flux in the forward direction and around 1 eV internal energy. This implies a suppression of the differential cross section in this range due to the vibrational excitation.

No chemical dynamics simulations are presently available for the dihalide channels. We therefore discuss the possible origin of the observed suppression based on our experimental results. While it is reasonable to assume that the FI⁻ channel forms by an F⁻ frontside attack on the iodine side, this is not likely to lead to FHI⁻ products by subsequent hydrogen insertion. Instead, FHI⁻ formation is rather expected to proceed by concerted or subsequent proton transfer and I⁻ abstraction. Such a reaction path makes this channel sensitive to CH-stretching excitation, which is in agreement with the observation that the dihalide suppression is dominated by the FHI⁻ pathway. The contribution of the FHI⁻ channel was previously found to rise up with increasing collision energy up to 2.3 eV and decreases above. This was interpreted as an instability effect, where additional internal excitation leads to dissociation of the intermediate complex. Adding energy via vibrational excitation could enhance this dissociation efficiently, which would explain the infrared suppression effect observed here.

In summary, we have probed the influence of the symmetric CH-stretching vibration on four different reaction pathways for the reaction of F⁻ with CH₃I in the collision energy range of 0.7–2.3 eV. We find all possible outcomes, namely, enhancement, suppression, and spectator mode behavior, for the different product channels in the same experiment. The SN₂ channel is not influenced at the two lowest collision energies but shows a 20% enhancement at 2.3 eV collision energy. This is in quantitative agreement with recent trajectory calculations by the Czakó group at the two lower collision energies and fits channels.

Figure 2. Relative change due to vibrational excitation for, from top to bottom, the SN₂, proton transfer, and halide abstraction channels. The first two are presented for the three investigated collision energies. The halide abstraction channels are open only at the highest collision energy, and instead the combined and individual differences are presented as described in the text.

Figure 3. Center of mass velocity distribution of FHI⁻ products for ground-state reactions (a) and for the difference of laser on and off (b). Also shown are the derived angular (c) and internal energy distributions (d).
the overall trend toward enhancement over the energy range they investigated. The proton transfer is enhanced over the entire collision range, and the enhancement is in qualitative agreement with SVP and QCT calculations. Finally, the two halide abstraction channels show an overall suppression that is dominated by the suppression of the FHI⁻ channel, possibly caused by an instability of an intermediate complex induced by the additional internal energy. To gain further insight into these dynamics, trajectory simulations at higher collision energies are highly desirable. The present experiment paves the way for searches of similar mode-specific dynamics in substitution reactions that are more direct, for example, involving Cl⁻ and CH₂I⁻ or that involve a competing elimination pathway as in F⁻ + CH₂I⁻.34

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01095.

Detailed description of the experimental procedures; additionally differential cross sections for the S₂,2 and the halide abstraction channel leading to FI⁻ channel; Figures S1–S5 as well as Table S1 (PDF)

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**Notes**

The authors declare no competing financial interest.

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