

RESEARCH ARTICLE | FEBRUARY 13 2024

Automated potential energy surface development and comprehensive dynamics for the $F + CH_3NH_2$ reaction

Tímea Szűcs ; Gábor Czako  



J. Chem. Phys. 160, 064304 (2024)

<https://doi.org/10.1063/5.0191398>



CrossMark



The Journal of Chemical Physics
2024 Emerging Investigators
Special Collection

Submit Today

Automated potential energy surface development and comprehensive dynamics for the $F + CH_3NH_2$ reaction

Cite as: J. Chem. Phys. 160, 064304 (2024); doi: 10.1063/5.0191398

Submitted: 13 December 2023 • Accepted: 18 January 2024 •

Published Online: 13 February 2024



Tímea Szűcs  and Gábor Czako^{a)} 

AFFILIATIONS

MTA-SZTE Lendület Computational Reaction Dynamics Research Group, Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged H-6720, Hungary

^{a)} Author to whom correspondence should be addressed: gczako@chem.u-szeged.hu

ABSTRACT

This work is an extensive investigation of the $F + CH_3NH_2$ reaction dynamics using a newly-developed potential energy surface (PES). The full-dimensional spin-orbit (SO) corrected (MRCI+Q/aug-cc-pwCVDZ) PES is developed by the ROBOSURFER program package and the ManyHF method is used in order to fix the Hartree-Fock (HF) convergence issues in the entrance channel. On the surface, retrieved by the fitting of the iteratively extended set of the ManyHF-CCSD(T)-F12a/triple-zeta-quality and SO-corrected energy points, quasi-classical trajectory (QCT) simulations are run. By analyzing the opacity functions and integral cross sections (ICSs) of six reaction channels, the dynamics of the two most reactive hydrogen-abstraction reactions resulting in $HF + CH_2NH_2/CH_3NH$ products are selected for a thorough examination. Despite the statistically and thermodynamically expected results, the kinetically preferred amino hydrogen-abstraction is the dominant mechanism at low collision energies. The initial attack angle and scattering angle distributions are investigated as well. The post-reaction energy distributions show that the collision energy mostly converts into the translational energy of the products, while the reaction energy excites the vibration of the products. The computed vibrationally resolved rotational distributions and vibrational state distributions of the HF product are compared to experimental data, and the theory and experiment are found to be in good agreement.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0191398>

I. INTRODUCTION

The experimental investigation of the dynamics of the reaction of the F atom with molecules^{1–11} continues to encourage the performance of theoretical studies,^{12–20} which can serve as a supplement to the experimental results. In the field of molecular dynamics, the collaboration between the experimental and theoretical approaches stands as a cornerstone for unraveling the intricacies of reaction dynamics and provides an understanding. Thorough experimental measurements accomplished by refined laser and high-resolution crossed molecular beam techniques can be compared to the most advanced-level theoretical quantum dynamics studies.²¹ Besides the various parameters that can be obtained by both approaches, most frequently the energy partitioning, the vibrational state distributions, or angular distributions of products are com-

pared. For example, in an old work, the vibrational branching for the HF product of the $F + H_2O \rightarrow HF + OH$ reaction was obtained theoretically by direct dynamics computational simulations¹³ in accordance with the experimental crossed jet reactive scattering dynamics.^{3,4} Since dynamics simulations require the determination of a huge amount of potential energy and gradient calculations, the available accuracy of direct dynamics is not satisfactory in some cases. Another common method of the description of the dynamics is the construction of an accurate potential energy surface (PES) by fitting analytically a database of high-quality *ab initio* energy points. This latter approach was used for quasi-classical trajectory (QCT) simulations for the $F + NH_3/ND_3$ systems by Espinosa-García and Monge-Palacios¹⁴ enabling the comparison of the energy partitioning, vibrational populations, and scattering angle distributions for the HF and DF products with experiments.^{5,6} The

PES-based QCT simulations have been applied for larger $F + CH_4$ and $F + C_2H_6$ systems as well,^{16–18} where the obtained HF vibrational and rotational populations are in excellent agreement with experiments.^{7,9}

In addition to the reactions of fluorine atom with the above-mentioned molecules, methylamine (CH_3NH_2) with two functional groups is also a good reactant candidate from the point of view of the reaction dynamics study. The present comprehensive theoretical investigation of the $F +$ methylamine dynamics, in addition to expanding our knowledge of such systems, is motivated by the fact that an analytical PES cannot be found for this reaction in the literature, while the dynamics of the two hydrogen-abstraction reaction channels have already been studied experimentally.^{10,11} Before our exhaustive PES characterization of the title reaction covering six reaction channels,²² Schaefer and co-workers¹⁹ also revealed theoretically the stationary points of the two hydrogen-abstraction reactions. The present study provides a CCSD(T)-F12a/triple-zeta-quality global full-dimensional analytical potential energy surface, which serves as a basis of the dynamics analysis. For the challenging PES development, we use the ROBOSURFER program package,²³ of which outstanding efficiency has been proven by several previous studies conducted by our research group,^{24–28} and the ManyHF method.²⁹ This latter is required in order to eliminate the Hartree–Fock (HF)³⁰ convergence problem occurring in the entrance channel avoiding the use of the multi-reference configuration interaction (MRCI) method³¹ (which provided a solution for the same issue in the case of the $F + C_2H_6$ system¹⁸). This pragmatic automated method was successfully applied to the dynamics analysis of the $Cl + CH_3NH_2$ reaction as well²⁰ to solve the HF problems in the reactant region. With the above-mentioned approaches, in addition to the useful results retrieved from the QCT simulations, we successfully compared the experimental data^{10,11} with theoretical ones for the first time for the hydrogen-abstraction reactions of the $F + CH_3NH_2$ system.

II. COMPUTATIONAL DETAILS

A. Development of the global potential energy surface

The implemented steps during the whole PES development process are represented in Fig. 1. For the fitting set construction, we utilized the structures and benchmark energies of the stationary points determined in our previous work for the $F + CH_3NH_2$ reaction.²² Considering the two functional groups of methylamine, the database consists of the points in the regions of the reactants, transition states, pre- and postreaction complexes, and products of the following channels:

1. Methyl hydrogen-abstraction (CH_3 HA, leading to $HF + CH_2NH_2$).
2. Amino hydrogen-abstraction (NH_2 HA, leading to $HF + CH_3NH$).
3. Methyl hydrogen-substitution (CH_3 HS, leading to $H + CH_2FNH_2$).
4. Amino hydrogen-substitution (NH_2 HS, leading to $H + CH_3NHF$).
5. Methyl-substitution (MS, leading to $CH_3 + NH_2F$).
6. Amino-substitution (AS, leading to $NH_2 + CH_3F$).

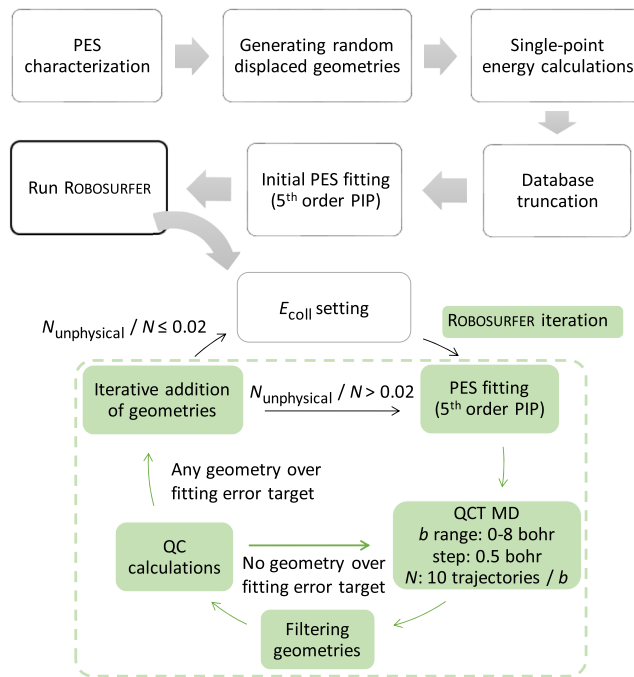


FIG. 1. Simplified flowchart of the potential energy surface development.

Starting from the most accurate geometries determined by the unrestricted explicitly-correlated coupled-cluster singles, doubles, and perturbative triples (UCCSD(T)-F12b) method³² and the correlation-consistent aug-cc-pVTZ basis set,³³ the important regions are described by a random displacement method.

The strategy is that we generate 500 structures in the entrance and each product channel, 250 geometries for the transition states, and pre- and post-reaction complexes by displacing the Cartesian coordinates by 0.00–0.32 Å. In addition, the species of the two-fragment systems are scattered around each other randomly in the 3–8 Å range.

The energies of the above-mentioned structures are obtained by single-point calculations applying the UCCSD(T)-F12a level of theory with the cc-pVDZ-F12³⁴ basis set. Moreover, considering the basis set correction, further computations are carried out at these points by the restricted explicitly-correlated second-order Møller–Plesset perturbation method (RMP2-F12)³⁵ with the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets as well. Because of HF-convergence problems in the reactant region, the HF wavefunction reference for the correlation methods is chosen by the ManyHF method; thus, the following composite energy single-point calculations are carried out for each geometry in the database:

$$E_{\text{composite}} = \text{ManyHF-UCCSD(T)-F12 a/cc-pVDZ-F12} \\ + (\text{ManyHF-RMP2-F12 /cc-pVTZ-F12} \\ - \text{ManyHF-RMP2-F12 /cc-pVDZ-F12}). \quad (1)$$

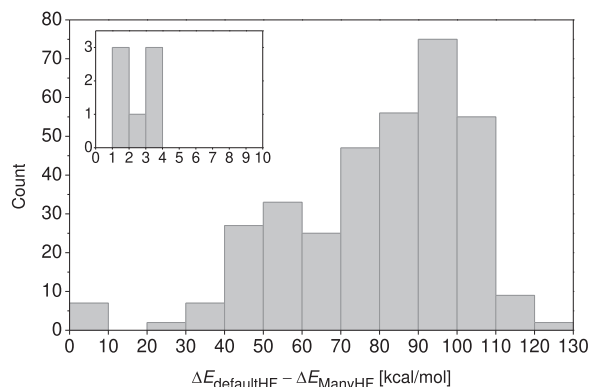


FIG. 2. Histogram of the errors of the default HF-based and ManyHF-based composite energies relative to the free reactants (kcal mol^{-1}) for 350 entrance-channel geometries of the $\text{F} + \text{CH}_3\text{NH}_2$ reaction.

As described in our previous work for the $\text{Cl} + \text{CH}_3\text{NH}_2$ reaction,²⁰ in the case of the title system also, a high-energy undesired excited-state wavefunction (and/or HF solution) is obtained by default (with default settings in MOLPRO 2015.1)³⁶ for many geometries in the reactant region. This HF convergence problem in the entrance channel may be related to the fact that three electronic states are close to each other in this region as shown in Fig. 4 in Ref. 22. This issue is solved by the ManyHF method that selects the HF solution leading to the deepest energy from several HF calculations that are started from different initial orbital sets. For 350 geometries, the deviations of the composite energies obtained by the default HF and ManyHF approaches are determined, and Fig. 2 shows the frequency of the differences. As can be seen, the $\Delta E_{\text{defaultHF}} - \Delta E_{\text{ManyHF}}$ values can even reach 10 kcal mol^{-1} ; moreover, 96.57% of the scrutinized cases are above this. The inset in the graph shows the $0\text{--}10 \text{ kcal mol}^{-1}$ interval of the difference in 1 kcal mol^{-1} increments, where we can see that all the seven cases in this region are above 1 kcal mol^{-1} ; thus, all of the obtained deviations are over the chemical accuracy. With the previous statements, it can be supported that the ManyHF method was indispensable for accurate PES development.

After the single-point energy calculations at the random displaced geometries, the database contains 7455 points. The chemically not relevant excessively high-energy region is neglected by discarding the geometries that have energy above $200 \text{ kcal mol}^{-1}$ relative to the global minimum of the fitting set. After the truncation, the database consists of 6014 *ab initio* energy points. The permutationally invariant polynomial (PIP)³⁷ method is used for the fitting, where the maximum order of the polynomial expansion is set to five, resulting in 5419 coefficients, which are obtained by a weighted linear least-squares fit. The weight of each point in the fitting set is defined as

$$w(E) = \begin{cases} 1, & \text{if } E \leq E_{\text{SlopeStart}}, \\ 1 + m \cdot (E - E_{\text{SlopeStart}}), & \text{if } E_{\text{SlopeStart}} < E \leq E_{\text{SlopeEnd}}, \\ w_{\text{SlopeEnd}} \cdot \frac{E_0}{E + E_0 - E_{\text{SlopeEnd}}} \cdot \frac{E_1}{E + E_1 - E_{\text{SlopeEnd}}}, & \text{if } E > E_{\text{SlopeEnd}}, \end{cases} \quad (2)$$

where E is the energy of the geometry relative to the reactants, $E_{\text{SlopeStart}}$ and E_{SlopeEnd} are the endpoints, $m = (w_{\text{SlopeEnd}} - 1)/(E_{\text{SlopeEnd}} - E_{\text{SlopeStart}})$ is the slope of the linearly decreasing section of the weight function, and w_{SlopeEnd} is the value of the weight where the function changes from linear to non-linear. The $w(E)$ is constant 1 up to $E_{\text{SlopeStart}}$, which is set to 35 kcal mol^{-1} , and it decreases linearly to 70 kcal mol^{-1} (E_{SlopeEnd}) relative energy, where its value is equal to 0.6 (w_{SlopeEnd}). The E_0 and E_1 are set to 0.1 and $0.5 E_h$, respectively, in the weight function of the highest energy region.

The quality of the PES is improved iteratively by the in-house ROBOSURFER program package. As shown in Fig. 1, at first, the collision energy is set (besides other important parameters during the configuration of the program), which is applied during the quasi-classical trajectory (QCT) simulations within the iterations. At the beginning, the collision energy (E_{coll}) is set to 10 kcal mol^{-1} . The PES retrieved from the database fitting in each iteration is used for the QCT computations. In this work, ten trajectories are run at each collision energy and impact parameter, and the latter is set from 0 to 8 bohr with 0.5 bohr increment. The geometries obtained from the reaction dynamics trajectories are filtered by a subprogram. Structures that may improve the PES are selected and quantum chemical (QC) inputs are generated automatically at the level of theory requested by the user. After the QC calculations, the outputs are analyzed by the program. If none of the successfully run cases have a fitting error above the fitting error target (here $E_{\text{threshold}}$ equals $0.5 \text{ kcal mol}^{-1}$), the cycle continues with dynamics simulations in order to generate new points. Otherwise, if any of the new geometries have a larger fitting error than $E_{\text{threshold}}$, after further filtering, the fitting set is iteratively expanded with these. Using underdeveloped PES results in reactive, non-reactive, and unphysical trajectories (where the energy of the products is not allowed) as well because some important regions are explored insufficiently. Therefore, by monitoring the number of unphysical trajectories, the degree of the development can be determined. In this study, if the ratio of these not-allowed cases relative to all trajectories is less than or equal to 2%, we consider that the development is done at the current collision energy. Then, the iteration is stopped, E_{coll} is increased, and the iterative procedure continues. Otherwise, a new ROBOSURFER iteration starts. For the $\text{F} + \text{CH}_3\text{NH}_2$ reaction, the development stopped at $100 \text{ kcal mol}^{-1}$ collision energy. The number of iterations is 47, 8, 3, 1, 4, 1, 5, 9, 4, and 8 at $E_{\text{coll}} = 10, 20, 30, 40, 50, 60, 70, 80, 90$, and $100 \text{ kcal mol}^{-1}$, respectively, i.e., 90 iterations are needed where 4539 energy points are added to the database; thus, the fitting set contains 10 553 geometries.

The accuracy of the resulting PES is enhanced by the consideration of the relativistic spin-orbit (SO) correction coming from the energy lowering by the fluorine atom. With the interacting-states approach,³⁸ where an active space of five electrons on three spatial 2p-like orbitals is used, the Davidson-corrected³⁹ all-electron multi-reference configuration interaction (MRCI+Q) method is utilized with the aug-cc-pwCVDZ basis set. The final potential energy of each point is calculated as

$$E_{\text{composite}} + \Delta_{\text{SO}}(\text{MRCI+Q}(5,3)/\text{aug-cc-pwCVDZ}), \quad (3)$$

where Δ_{SO} is the deviation between the SO_1 and non- SO_1 ground-state potential energies. Finally, the coefficients of the fifth-order polynomial are obtained by fitting the SO-corrected 10 548

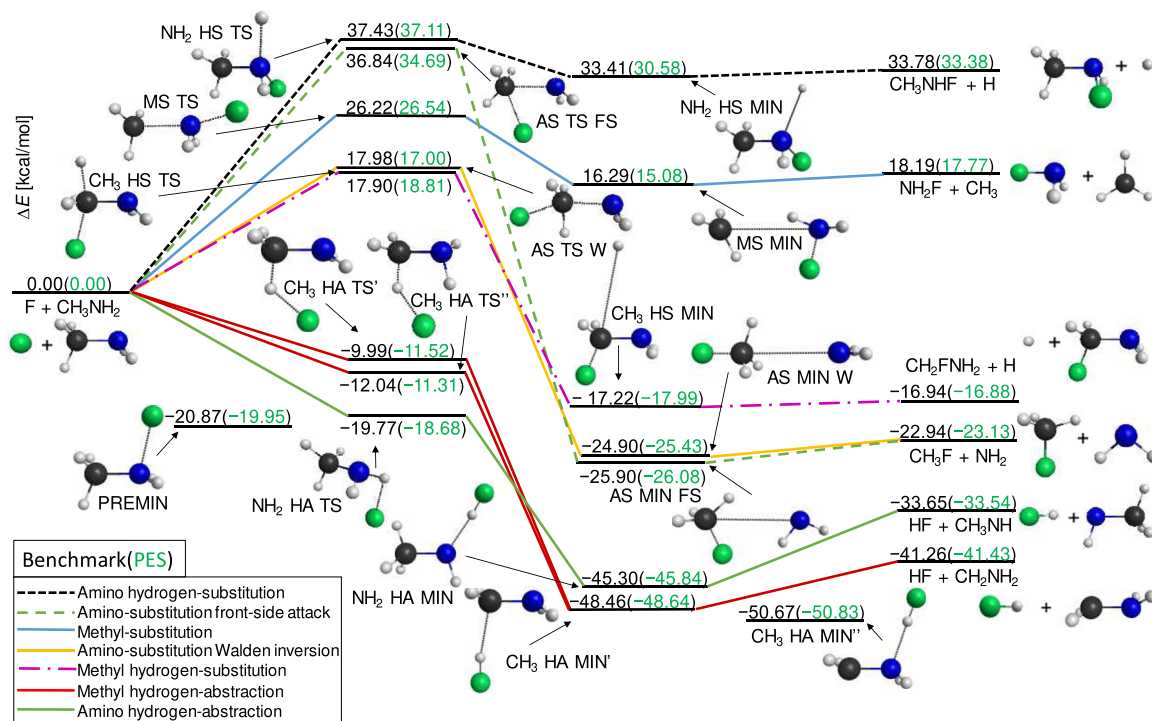


FIG. 3. Schematic potential energy diagram of the six reaction channels of the $F + CH_3NH_2$ reaction. The benchmark classical potential energies [obtained by Eq. (4), taken from Ref. 22] are determined at the represented CCSD(T)-F12/aug-cc-pVTZ geometries, and the PES potential energies are obtained for the PES-optimized structures (except the asterisk labeled ones, where the PES potential energies are determined at the CCSD(T)-F12/aug-cc-pVTZ geometries), where each value is relative to the reactants (given in kcal mol⁻¹). PREMIN is not connected because it can perform an important role in multiple pathways.

ab initio energy points (in five cases, MCSCF convergence problems occurred).

B. QCT simulations

The reaction dynamics of the $F + CH_3NH_2$ system is investigated by the quasi-classical trajectory method using the newly-developed PES. With normal-mode sampling,⁴⁰ zero-point energy is given to the methylamine reactant in order to set the initial vibrational energy of the system to the ground vibration state. In this study, the number of investigated trajectories is 800 000 altogether, which results from 5000 at each impact parameter (b) and collision energy: 1, 5, 10, 20, 30, 40, 50, and 60 kcal mol⁻¹. The b takes values from 0.0 to b_{max} with steps of 0.5 bohr, where, at b_{max} , the reaction probability vanishes. The initial distance setup between the two reactants is determined as $\sqrt{x^2 + b^2}$, where x equals 18.90 bohr. In our simulations, the end of the trajectory is reached when there is an interatomic distance that is 1 bohr larger compared to the initial largest one. The time step is 0.0726 fs (three atomic units) during the trajectory propagations.

III. RESULTS AND DISCUSSION

A. Energetics of the PES

As shown in Fig. 3, we investigate four exothermic and two endothermic pathways for the title reaction. The schematic energy

diagram represents the benchmark classical (retrieved from our previous work²²) and PES-optimized energies of the stationary points, relative to the reactants. The former is obtained as follows:

$$\begin{aligned} \Delta E_{\text{benchmark}} = & \text{CCSD(T)-F12b/cc-pV5Z-F12} \\ & + \delta[\text{CCSDT}] + \delta[\text{CCSDT(Q)}] + \Delta_{\text{core}} \\ & + \Delta_{\text{rel}} + \Delta_{\text{SO}}, \end{aligned} \quad (4)$$

where the CCSD(T)-F12b/cc-pV5Z-F12 energies, the post-(T) correlation energies ($\delta[\text{CCSDT}]$, $\delta[\text{CCSDT(Q)}]$), the core correlation corrections (Δ_{core}), the scalar relativistic effects (Δ_{rel}), and the spin-orbit corrections (Δ_{SO}) are obtained at the CCSD(T)-F12b/aug-cc-pVTZ geometries with single-point energy calculations (detailed in Ref. 22). Considering the reactions of the methyl and amino groups, the two hydrogen-abstraction mechanisms (CH_3 HA and NH_2 HA) leading to $HF + CH_2NH_2$ and $HF + CH_3NH$ are barrierless and these are the most exothermic pathways, although the CH_3 HA is more exothermic with a reaction energy of -41.43 kcal mol⁻¹. Except in the case of the transition state of the amino hydrogen-abstraction, the absolute differences between the benchmark energies and the PES-obtained values of the stationary points for these channels are well below the root-mean-square (rms) error, which is 1.07 kcal mol⁻¹ in the $[-50.83, 35.00]$ kcal mol⁻¹ energy region. The pre-reaction complex in the entrance channel and the post-reaction complex in the

TABLE I. Integral cross sections (branching ratios) for the six product channels of the F + CH₃NH₂ reaction (bohr²) at eight collision energies (E_{coll} in kcal mol⁻¹).

E_{coll}	CH ₃ HA ^a	NH ₂ HA ^b	CH ₃ HS ^c	NH ₂ HS ^d	AS ^e	MS ^f
1	79.664 (0.20)	325.983 (0.80)	0.000 (0.00)	0.000 (0.00)	0.000 (0.00)	0.000 (0.00)
5	72.304 (0.40)	108.938 (0.60)	0.000 (0.00)	0.000 (0.00)	0.000 (0.00)	0.000 (0.00)
10	65.761 (0.43)	86.844 (0.57)	0.000 (0.00)	0.000 (0.00)	0.000 (0.00)	0.000 (0.00)
20	60.120 (0.46)	70.057 (0.54)	0.000 (0.00)	0.000 (0.00)	0.003 (0.00)	0.000 (0.00)
30	58.275 (0.49)	59.607 (0.51)	0.001 (0.00)	0.000 (0.00)	0.005 (0.00)	0.000 (0.00)
40	57.329 (0.52)	52.975 (0.48)	0.016 (0.00)	0.002 (0.00)	0.003 (0.00)	0.000 (0.00)
50	57.155 (0.55)	47.638 (0.45)	0.050 (0.00)	0.003 (0.00)	0.018 (0.00)	0.000 (0.00)
60	55.754 (0.56)	43.962 (0.44)	0.198 (0.00)	0.036 (0.00)	0.022 (0.00)	0.000 (0.00)

^a Methyl hydrogen-abstraction.^b Amino hydrogen-abstraction.^c Methyl hydrogen-substitution.^d Amino hydrogen-substitution.^e Amino-substitution.^f Methyl-substitution.

product channel (the global minimum of the PES) are also well described with 0.92 and 0.16 kcal mol⁻¹ $|\Delta E_{\text{benchmark}} - \Delta E_{\text{PES}}|$ absolute deviations, respectively. The amino-substitution and the methyl hydrogen-abstraction pathways are exothermic as well; however, they have high energy barriers. The former can proceed via Walden-inversion (AS TS W) and front-side-attack mechanisms (AS TS FS) with $\Delta E_{\text{benchmark}}(\Delta E_{\text{PES}}) = 17.98(17.00)$ and $36.84(38.13)$ kcal mol⁻¹, respectively. The relative energies of the AS FS and the amino hydrogen-substitution (NH₂ HS) transition states are in the [35.00, 62.75] kcal mol⁻¹ energy region, where the rms error is 1.42 kcal mol⁻¹. With the 0.52 kcal mol⁻¹ average absolute difference between the $\Delta E_{\text{benchmark}}$ and ΔE_{PES} energies, we can state that the newly-developed fifth-order analytical potential energy surface describes the title multi-channel system excellently.

B. Reaction probabilities and integral cross sections

The dynamics of the F + CH₃NH₂ reaction is evaluated by analyzing the coordinates and the velocity vectors of the reactants and products at the beginning and at the end of each trajectory. The first step is the classification of the trajectories, where the six reaction channels, non-reactive, and unphysical categories are considered. In Table I, the integral cross sections (σ) are indicated for the six reaction channels. The σ is the b -weighted integral of the opacity function $P(b)$, which is the reaction probability as a function of the b impact parameter (see Fig. 4). It can be seen that the two hydrogen-abstraction channels occur at all collision energies applied for the dynamics simulations. Even though the CH₃ HS, NH₂ HS, and AS pathways open at 30, 40, and 20 kcal mol⁻¹ collision energies, respectively, their σ values are negligible compared to the values determined for the CH₃/NH₂ HA reaction channels. The methyl-group substitution is not observed at any collision energy. The negligible reactivity of the substitution channels may be explained by their presumably narrower transition-state attack angle range and by the fact that the HA pathways are barrierless and much more competitive than the HS and AS channels. Due

to the low reaction probability (thus, large statistical errors) of the substitution channels, a more detailed investigation is done for the hydrogen-abstraction reactions. Surprisingly, the NH₂ HA occurs more frequently than the CH₃ HA at $E_{\text{coll}} < 30$ kcal mol⁻¹, as the σ of the former is 4.1, 1.5, 1.3, and 1.2 times larger at 1, 5, 10, and 20 kcal mol⁻¹ collision energies, respectively. It can be explained by the fact that the transition state of the former pathway has ~ 8 kcal mol⁻¹ deeper relative energy; however, thermodynamically and statistically (considering the number of hydrogen atoms of the functional groups), this finding is less expected. In the case of the Cl + CH₃NH₂ reaction, the opposite is realized, where the methyl hydrogen-abstraction has at least 2.6 times larger integral cross section at all collision energies.²⁰ Table I also shows that this ratio is around 1:1 at $E_{\text{coll}} = 30$ kcal mol⁻¹ for the title reaction and the hydrogen-abstraction from the methyl group is slightly more favorable beyond this.

The above-mentioned statements are reflected in Fig. 4 as well, where the integral cross sections (ICSSs) as a function of the collision energy, and the opacity functions are represented for the two hydrogen-abstraction channels. In addition, soft and hard zero-point energy restrictions are applied for the ICSSs. In the soft case, only trajectories that fulfill the conditions indicated by Eq. (5) or (6) are considered, and in the hard case, Eqs. (7) and (8) must be accomplished.

Soft:

$$\text{CH}_3 \text{ HA: } E_{\text{vib}}(\text{CH}_2\text{NH}_2) + E_{\text{vib}}(\text{HF}) > \text{ZPE}(\text{CH}_2\text{NH}_2) + \text{ZPE}(\text{HF}), \quad (5)$$

$$\text{NH}_2 \text{ HA: } E_{\text{vib}}(\text{CH}_3\text{NH}) + E_{\text{vib}}(\text{HF}) > \text{ZPE}(\text{CH}_3\text{NH}) + \text{ZPE}(\text{HF}). \quad (6)$$

Hard:

$$\begin{aligned} \text{CH}_3 \text{ HA: } E_{\text{vib}}(\text{CH}_2\text{NH}_2) &> \text{ZPE}(\text{CH}_2\text{NH}_2) \\ \text{and} \\ E_{\text{vib}}(\text{HF}) &> \text{ZPE}(\text{HF}), \end{aligned} \quad (7)$$

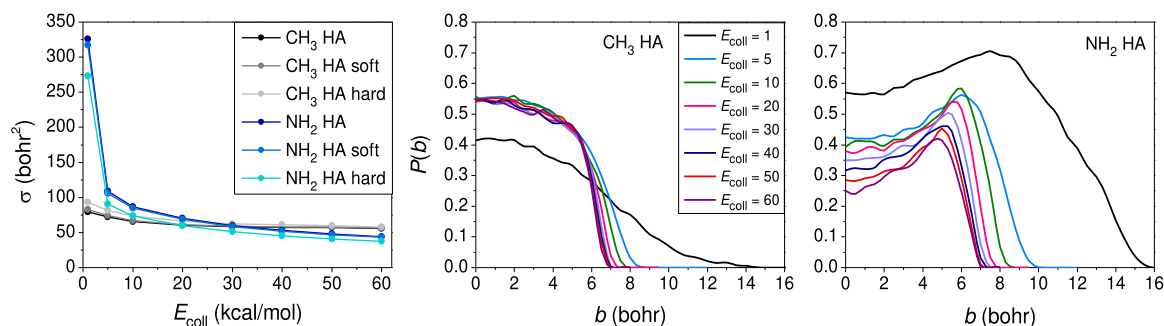


FIG. 4. Integral cross sections [with and without zero-point energy restrictions, see Eqs. (5)–(8)] as a function of the collision energy (left) and reaction probabilities as a function of the impact parameter for the methyl (middle) and amino (right) hydrogen-abstraction channels of the $\text{F} + \text{CH}_3\text{NH}_2$ reaction at the applied collision energies (in kcal mol^{-1}).

$$\text{NH}_2 \text{ HA: } E_{\text{vib}}(\text{CH}_3\text{NH}) > \text{ZPE}(\text{CH}_3\text{NH})$$

and

$$E_{\text{vib}}(\text{HF}) > \text{ZPE}(\text{HF}). \quad (8)$$

As both reactions have submerged barriers, it is expected that the ICSs decrease with increasing collision energy. This effect is more significant in the case of the abstraction from the amino group, mainly from 1 to 5 kcal mol^{-1} collision energies, where the ICSs decrease to around 1/3. Due to the high exothermicity of these reactions, the integral cross sections do not change significantly with the ZPE constraints. The values change differently in the case of the two channels. For NH_2 HA, ICSs decrease for soft and hard constraints, whereas the constraints somewhat surprisingly increase the ICSs for the other reaction. This is because, in the CH_3 HA case, the ZPE violation is less significant and the ZPE violating trajectories of both reactions are rejected, which decreases the total number of trajectories, thereby increasing the reactivity of the CH_3 HA channel.

Apart from the $E_{\text{coll}} = 1 \text{ kcal mol}^{-1}$ results, the methyl hydrogen-abstraction shows weak collision energy dependence, in contrast to the amino hydrogen-abstraction, whose probability clearly decreases with increasing E_{coll} (see Fig. 4). CH_3 HA prefers the nearly frontal collision, where the impact parameter is 0, and with increasing b , a continuous decrease in the $P(b)$ can be observed. In contrast, the probabilities increase with b and these have maximum at higher impact parameter values in the NH_2 HA case, which suggests a forward-scattering stripping mechanism at each collision energy. At lower E_{coll} , there are higher b_{max} (where probability is zero) values because the velocity of the reactants is lower, i.e., the available time allows the interactions between the two reactants to force the correct orientation, thus increasing the reactivity. The higher collision energies result in lower b_{max} values since the higher velocity of the reactants does not allow sufficient time to attract the reactants close to each other from a long distance and to achieve the appropriate orientation.

C. Initial attack angle and scattering angle distributions and energy distributions of the products

The orientation of the reactants is randomly sampled at the beginning of each trajectory. Therefore, the distributions of the

initial attack angle of the reactive collisions are scrutinized. The α is defined as the angle of the N–C vector and the center of the mass velocity vector of the methylamine reactant (see Fig. 5). The $\cos(\alpha) = -1$ corresponds to the attack of the fluorine atom from the side of the methyl group in line with the C–N bond and the $\cos(\alpha) = 1$ case is the amino-group-side attack. All determined $\cos(\alpha)$ values are assigned to one of the ten equidistant bins in the -1 to 1 range. At low collision energies, the $\alpha = 0^\circ$ is not the preferred approaching direction in the case of the methyl hydrogen-abstraction, as the largest differential cross section (DCS) values are displayed at the $\alpha = 80^\circ$ – 60° , 70° – 50° , and 60° – 45° ranges at $E_{\text{coll}} = 1, 5$, and 10 kcal mol^{-1} , respectively. At higher collision energies, the CH_3 HA favors the C-side attacking in line with the C–N bond. In the case of the amino hydrogen-abstraction, the distributions show less dependence on the collision energy, and the attack from the N atom, in line with the C–N bond, is the most favorable in all cases. However, at higher energies, the distributions are more isotropic and the collisions are reactive even in the case of the side approach; however, for $E_{\text{coll}} = 40$ – 60 kcal mol^{-1} from $\cos(\alpha) = -1.0$ to 0.0 , the normalized DCS values are around 0.6 .

Evaluating the angle of the velocity vectors of the center of masses of the reactants and products leads to the scattering angle (θ) distributions (see Fig. 5). The θ is defined as $\theta = 0^\circ$ that corresponds to the forward scattering and the $\theta = 180^\circ$ case that indicates the backward scattering. The -1 to 1 range of $\cos(\theta)$ is divided into ten equidistant bins and each obtained value is assigned to one of these (as for the attack angle distributions). In both reactions, the forward-scattering prevails at all collision energies, indicating a stripping mechanism. However, at lower collision energies, the products' scattering is more isotropic (due to the complex formation), and with increasing E_{coll} , the direction preference appears; the mechanism is more direct. By examining the animations of selected trajectories, we have observed that, at lower collision energies, the HF product is formed along the hydrogen-abstraction pathway through the transition state and product-like MIN complex(es); however, the HF and CH/NH bonds alternately lengthen and shorten multiple times until fluorine finally abstracts the hydrogen. Furthermore, in the case of CH_3 HA, the HF fragment often forms a hydrogen bond with the N atom before separation. At higher collision energies, after the HF bond formation, the products separate

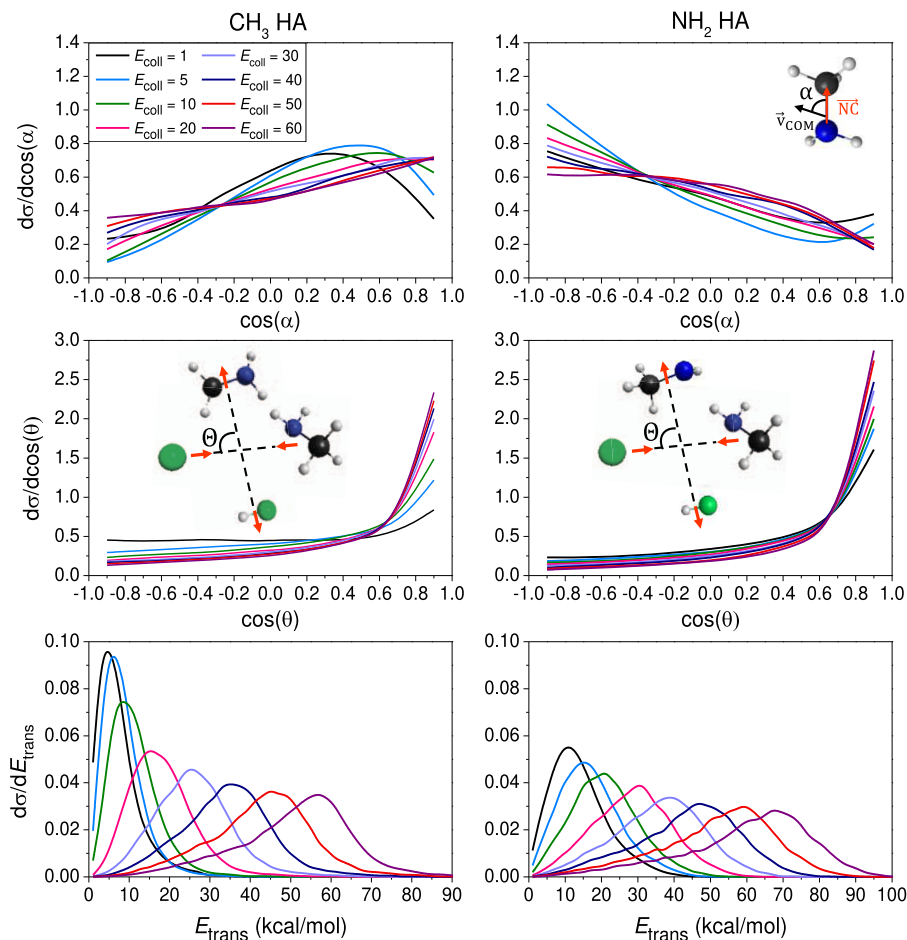


FIG. 5. Normalized distributions of the initial attack angle (first row), scattering angle (second row), and relative translational energy of the products (third row) determined for the methyl (left column) and amino (right column) hydrogen-abstraction channels of the $\text{F} + \text{CH}_3\text{NH}_2$ reaction at eight collision energies (kcal mol^{-1}).

promptly. In consistent with the observation at the opacity functions, where the distributions have a maximum at around the b_{max} in the case of the NH_2 HA reaction, the preference of the forward-scattering becomes more significant for the abstraction from the amino-group.

In Fig. 5, the relative translational energy of the products (E_{trans}) can be seen as well for the amino and the methyl hydrogen-abstraction reactions. At each E_{coll} , the energy region between the minimum and maximum E_{trans} values is divided into 2 kcal mol^{-1} equidistant bins, and the relative translational energy of the products of each trajectory is assigned to the corresponding bin. Then, a cross section is computed for each bin. For both reactions, the distributions have a maximum at each collision energy, which appears at the value near the applied E_{coll} for the $\text{HF} + \text{CH}_2\text{NH}_2$ products and at 10 kcal mol^{-1} higher than the E_{coll} in the case of the $\text{HF} + \text{CH}_3\text{NH}$ products. This indicates that the E_{trans} transfers efficiently from the reactants to the products. The left-to-right shifting of the maximum of the curves with increasing collision energy shows the previously mentioned mechanism shifting from indirect

to direct. This can be supported by the fact that, at lower collision energies, complexes are formed and the products separate with less translational energy, unlike in the case of the direct mechanism, where the products have higher E_{trans} .

Normalized product internal (E_{int}), vibrational (E_{vib}), and rotational (E_{rot}) energy distributions of the CH_3 HA and NH_2 HA reactions can be found in Figs. 6 and 7, of which the former illustrates the energy distributions of the HF product of both channels, whereas the latter refers to CH_2NH_2 and CH_3NH . The internal energy splitting to the vibrational and rotational energies is based on the E_{rot} determination by the rigid rotor approximation and E_{vib} is defined as $E_{\text{int}} - E_{\text{rot}}$. In all cases (E_{int} , E_{vib} , E_{rot}), the binning at each E_{coll} is performed as described for E_{trans} . The collision energy dependence of the E_{int} distributions of all products is less than in the case of the above-mentioned translational energy, suggesting a more efficient transform from E_{coll} to E_{trans} . (The average values of the relative translational, vibrational, and rotational energy of the products for the two hydrogen-abstraction reaction channels are represented in Table II.) The reactions of both methyl and amino

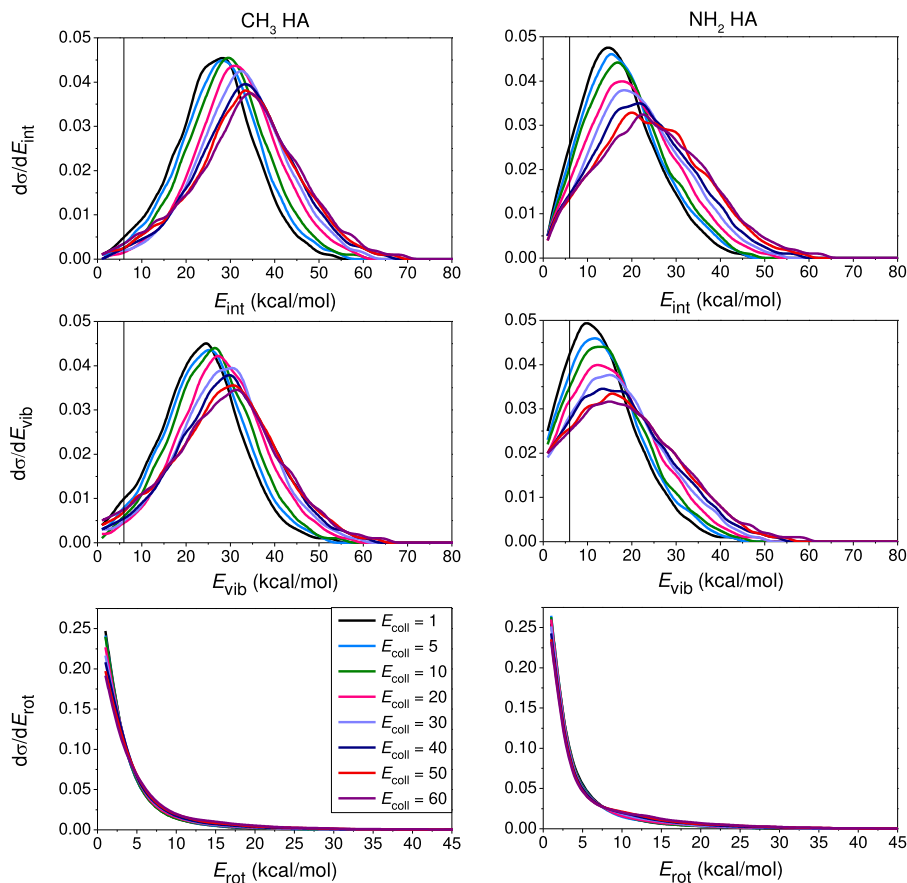


FIG. 6. Normalized distributions of the internal (first row), vibrational (second row), and rotational (third row) energy of the methyl (left column) and amino (right column) hydrogen-abstraction-formed HF molecule in the $F + \text{CH}_3\text{NH}_2$ reaction at the eight applied collision energies (kcal mol^{-1}). The zero-point energy value of HF is indicated by the vertical lines.

groups are exothermic and the released energy flows into the internal energy of the products. The $\Delta E_{\text{benchmark}}(\Delta E_{\text{PES}})$ is $-33.65(-33.54)$ and $-41.26(-41.43)$ kcal mol^{-1} for the amino and methyl hydrogen-abstractions, respectively, and this nearly 8 kcal mol^{-1} difference of the relative energies can be observed in both the E_{int} and E_{vib} distributions of the products. The ZPE values of HF, CH_2NH_2 , and CH_3NH are indicated in Figs. 6 and 7, and it can be seen that the ZPE violations are small due to the exothermicity of the reactions. A significant portion of the internal energy originates from the vibration of the products, which is expected since the HF bond is elongated by 0.6–0.7 Å in the structures of the transition states of these early-barrier pathways compared to the equilibrium HF product structure. Thus, vibrationally excited products are formed. The collision energy dependence of the internal energy distributions mainly originates from the HF vibration since the rotation is much less dependent on E_{coll} . On the other hand, in the case of the polyatomic products, the E_{coll} dependence is due to the rotation of the CH_2NH_2 and CH_3NH molecules since the decay of the E_{rot} distributions is more and more extended with increasing collision energy.

D. Rotational quantum number value and vibrational state distributions of the HF product

The rotational quantum number value (J) distributions, i.e., normalized J -specific cross sections, of the HF product originating from the methyl and amino hydrogen-abstraction reactions are investigated in this work (Fig. 8), also considering the vibrationally resolved J distributions (Fig. 9). The results with ZPE restrictions are not presented here since, as described above in the examination of E_{int} and E_{vib} , the ZPE violation is slight for these two reaction channels, especially for CH_3 HA. (Note that we have checked the J distributions for both channels with ZPE restrictions, but the results have been found very similar with and without the constraints.) The collision energy dependence of the distributions is not significant, but a modest blue shifting of the curves' maximum can be observed with increasing E_{coll} . The most populated levels are in a slightly more extended range for the CH_3 HA ($J = 4$ – 7) compared to the NH_2 HA ($J = 3$ – 5). In Fig. 9, the DCSs of the J values are shown for the HF product at $E_{\text{coll}} = 5$ kcal mol^{-1} originating from the two hydrogen-abstraction reactions. It can be seen that, at higher vibrational states, the rotation of the HF is not much colder, and the

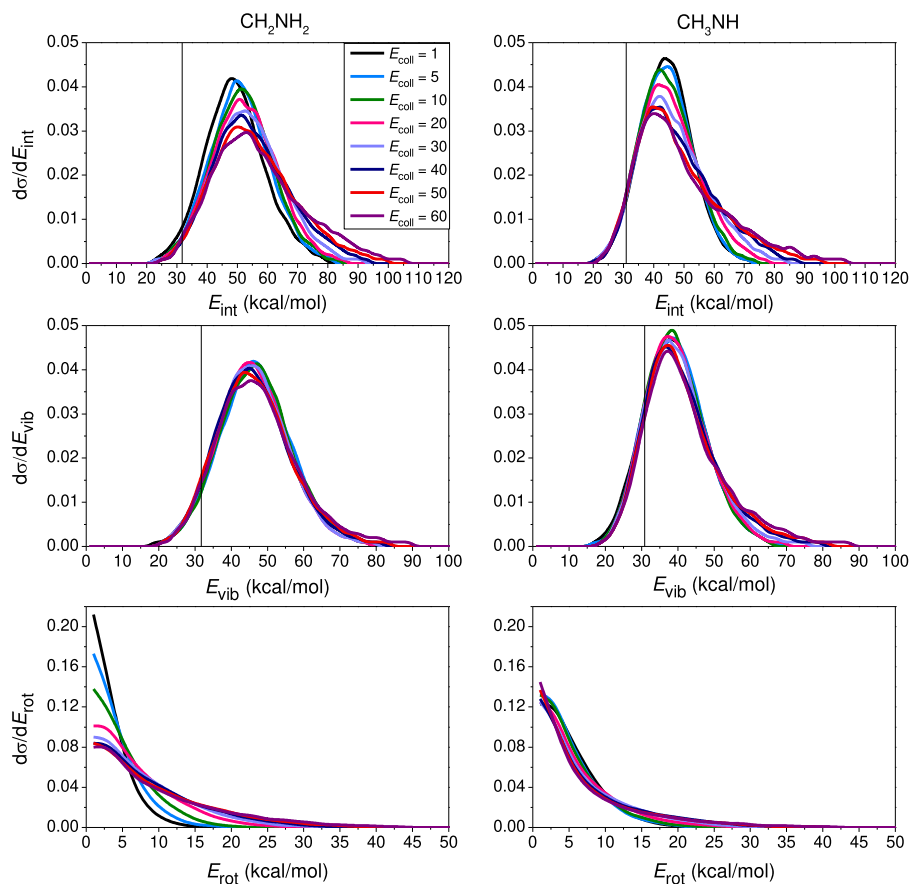


FIG. 7. Normalized distributions of the internal (first row), vibrational (second row), and rotational (third row) energy of the CH_2NH_2 (left column) product of the methyl hydrogen-abstraction and of the CH_3NH (right column) product of the amino hydrogen-abstraction in the $\text{F} + \text{CH}_3\text{NH}_2$ reaction at the eight applied collision energies (kcal mol^{-1}). The zero-point energy values of the molecules are indicated by the vertical lines.

TABLE II. Average values of the relative translational (E_{trans}), vibrational (E_{vib}), and rotational (E_{rot}) energy of the products for the methyl (CH_3 HA) and amino (NH_2 HA) hydrogen-abstraction channels of the $\text{F} + \text{CH}_3\text{NH}_2$ reaction at eight collision energies (kcal mol^{-1}).

E_{coll}	E_{trans}	CH ₃ HA				NH ₂ HA				
		E_{vib}^a		E_{rot}		E_{trans}	E_{vib}^a		E_{rot}	
		HF	CH ₂ NH ₂	HF	CH ₂ NH ₂		HF	CH ₃ NH	HF	CH ₃ NH
1	7.37	23.12	46.07	3.46	3.16	13.90	13.32	39.43	3.71	4.97
5	8.37	24.16	47.14	3.69	3.89	17.05	14.22	39.45	3.78	4.85
10	11.24	25.59	46.92	3.72	4.85	21.08	14.98	39.13	3.84	5.03
20	17.99	27.74	46.02	3.94	6.53	28.43	16.40	39.33	4.04	5.74
30	26.00	28.58	46.02	4.17	7.61	35.72	17.29	40.03	4.41	6.36
40	34.25	28.87	46.05	4.46	8.44	43.45	18.09	40.99	4.82	6.86
50	42.69	28.89	46.40	4.92	9.06	51.52	18.94	41.07	5.31	6.74
60	50.96	28.79	47.26	5.34	9.62	59.88	19.38	41.73	5.63	6.87

^a E_{vib} is relative to the corresponding product minimum.

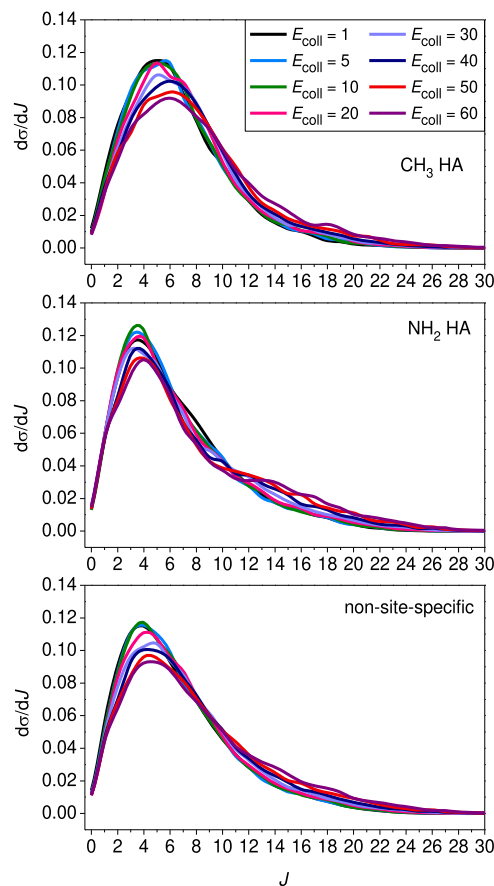


FIG. 8. Normalized distributions of the HF product's rotational quantum number value (J) of the methyl (top) and amino (middle) hydrogen-abstraction channels of the $F + \text{CH}_3\text{NH}_2$ reaction and of the two channels (bottom, the HF provenance is not distinguished) at the eight applied collision energies (kcal mol^{-1}).

rotational excitation of the molecule decreases with increasing vibrational quanta (ν), but the effect is not radical. The mean of the DCS values in the $J = 8\text{--}22$ range is higher by 0.011 for $\nu = 0$ than for $\nu = 3$ in the case of the CH_3 HA-resulted HF and by 0.016 for the NH_2 HA-resulted HF.

The vibrational-state distributions of the HF molecule are shown in Fig. 10 at eight collision energies for the two hydrogen-abstraction reactions. As expected from the above-mentioned statements of the elongated H–F bond in the transition states, the HF molecule is formed in vibrationally excited states. The most populated level is the $\nu = 2$ in the CH_3 HA case (in consistent with the observations made for the $F + \text{C}_2\text{H}_6$ reaction),¹⁸ while for the NH_2 HA reaction, the $\nu = 0$ and 1 states have the highest probability. This means that the HF product is less excited vibrationally in the latter case (since the reaction energy released is less for NH_2 HA), which is also seen in the case of vibrational energy distributions. With increasing collision energy, HF is more excited since, in the non-site-specific case at $E_{\text{coll}} = 1 \text{ kcal mol}^{-1}$, the most populated level is $\nu = 1$, while at $E_{\text{coll}} = 60 \text{ kcal mol}^{-1}$, the $\nu = 2$

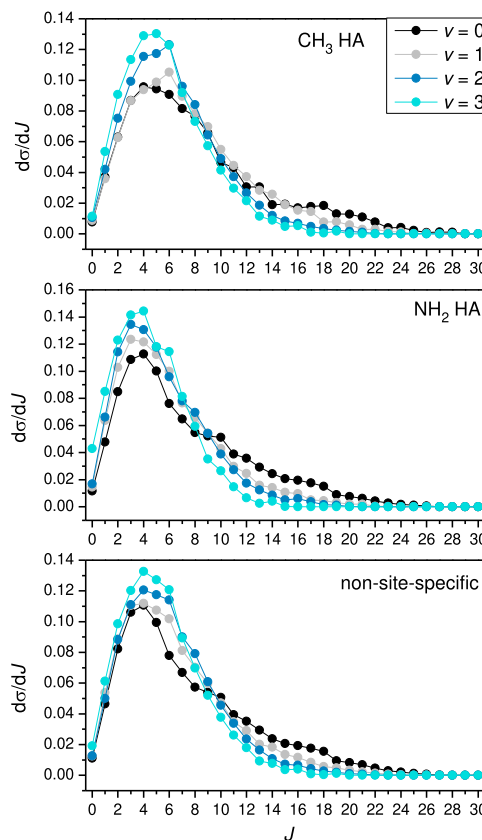


FIG. 9. Vibrationally resolved normalized distributions ($E_{\text{coll}} = 5 \text{ kcal mol}^{-1}$) of the HF product's rotational quantum number value (J) of the methyl (top) and amino (middle) hydrogen-abstraction channels of the $F + \text{CH}_3\text{NH}_2$ reaction and of the two channels (bottom, the HF provenance is not distinguished).

is the most populated. The HF excitation by 1 quantum requires $\sim 12 \text{ kcal mol}^{-1}$ energy; thus, the $\nu = 4$ and 5 levels are more populated at higher E_{coll} and in the case of the CH_3 HA, which is more exothermic. At low collision energies, the small populations of these levels are often due to the ZPE violation of the co-product.

E. Comparison with experiments

The vibrationally resolved rotational quantum number value (J) distributions of the HF product produced by the methyl hydrogen-abstraction reaction at 5 kcal mol^{-1} collision energy are compared to experimental data published by Wategaonkar and Setser¹¹ (see Fig. 11). The distinction of the two functional group reactions is achieved by deuterium substitution of the H atoms in the NH_2 -group in the experiments, resulting in CH_3ND_2 reactant. In the experimental article, the reported results are gained from two experimental methods: fast flow reactor (FR) and arrested relaxation (AR), where the latter data are measured by Wassell and co-workers.¹⁰ Our simulations are in good agreement with the measurements by the AR method, but the distributions determined by the theoretical

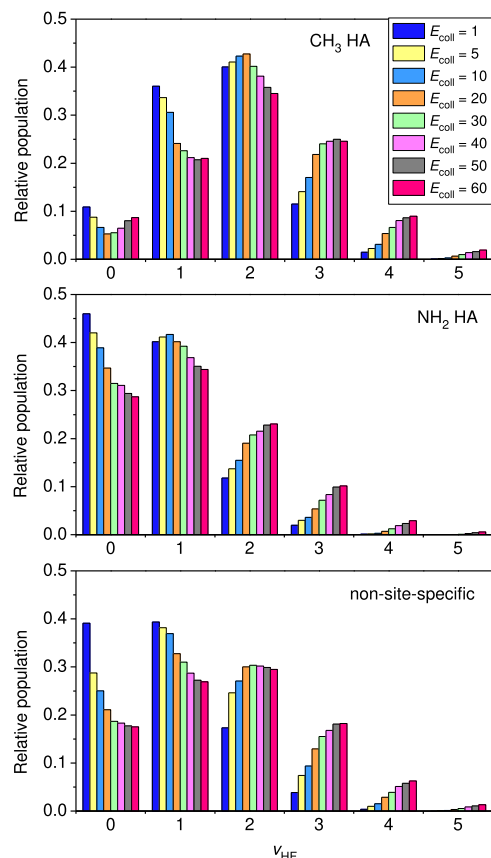


FIG. 10. Normalized vibrational state distributions of the HF product originating from the methyl (top) and amino (middle) hydrogen-abstraction channels of the $F + CH_3NH_2$ reaction and of the two channels (bottom, the HF provenance is not distinguished) at eight collision energies (kcal mol^{-1}).

calculations are slightly shifted to higher J values. The finding that the present theoretical results agree better with the AR experimental data is expected since the arrested relaxation studies are done in an

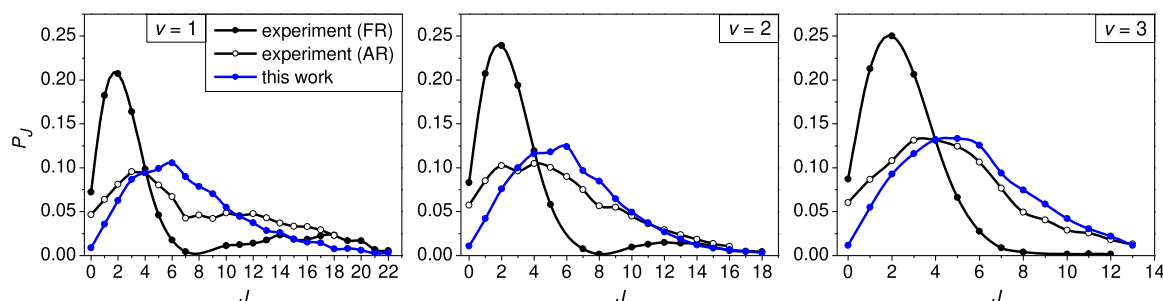


FIG. 11. Theoretical ($E_{\text{coll}} = 5 \text{ kcal mol}^{-1}$) and experimental normalized rotational quantum number (J) distributions for the $v = 1, 2$, and 3 vibrational states of the HF product originating from the methyl hydrogen-abstraction channel of the $F + CH_3NH_2(\text{theory})/CH_3ND_2(\text{experiment})$ reaction. The FR and AR experimental results are acquired from Ref. 11 (normalized in this work), which correspond to the data obtained by the fast flow reactor method and the arrested relaxation method, respectively. (AR measurements were originally reported in Ref. 10.).

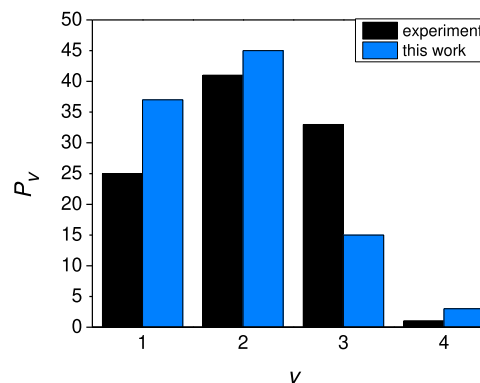


FIG. 12. Theoretical ($E_{\text{coll}} = 5 \text{ kcal mol}^{-1}$) and experimental (Ref. 11) vibrational state distributions (normalized to 100) of the HF product originating from the methyl hydrogen-abstraction channel of the $F + CH_3NH_2(\text{theory})/CH_3ND_2(\text{experiment})$ reaction.

effort to prevent experimental difficulties associated with relaxation and secondary reactions to obtain nascent HF distributions.

In Ref. 11, the vibrational state distribution of the HF product originating from the CH_3 HA reaction was reported, enabling the comparison with the theoretical data obtained in this work at $E_{\text{coll}} = 5 \text{ kcal mol}^{-1}$ as shown in Fig. 12. For the $v = 1, 2, 3$, and 4 , the experimentally determined P_v values (normalized to 100) are 25 ± 1 , 41 ± 1 , 33 ± 1 , and 1 ± 0.2 , respectively, and $37, 45, 15$, and 3 are the corresponding theoretical results. In both cases, the most populated level is $v = 2$ and the least populated is $v = 4$.

IV. SUMMARY AND CONCLUSIONS

A full-dimensional spin-orbit-corrected PES is developed for the $F + CH_3NH_2$ reaction using the ROBOSURFER program package and the fifth-order permutationally invariant polynomial method for fitting. For the calculations of the *ab initio* energy points constructing the fitting set, the ManyHF method is used for handling the HF convergence problems in the reactant region, where the default

HF method implemented in the MOLPRO program package determines absurdly high energies. For the development, the ManyHF-UCCSD(T)-F12a/cc-pVDZ-F12 level of theory is applied with basis set correction of cc-pVTZ-F12–cc-pVDZ-F12 at the RMP2-F12 level of theory. Quasi-classical dynamics simulations are performed on the new PES. Reaction probabilities and integral cross sections show that the two exothermic H-abstraction pathways are the most reactive of the six investigated channels. Further analysis is performed for these two reactions, including the initial attack angle, scattering angle, product translational energy, and post-reaction energy distributions. The first of these shows that the hydrogen-abstraction occurs on the functional-group that is approached by the fluorine atom in line with the C–N bond, or in the case of the methyl H-abstraction, the side-attack is reactive as well. From the scattering angle distributions, we can conclude that, with increasing collision energy, the forward scattering is getting more common. Most of the collision energy flows into the relative translational energy of the products, and a slight amount excites the rovibrational modes. Due to the elongated H–F bond at the transition states, and the exothermicity of the reactions, the produced HF molecule is vibrationally excited. The rotational quantum number value distributions of the HF product are examined as well, where the HF J values in the case of the CH₃-side reaction are slightly blue-shifted, but the difference between the two reactions is not significant, not even with the vibrational state resolution. The J value distributions obtained in this work at $v = 1, 2$, and 3 states for the HF originating from the CH₃ HA are in consistent with the experimental data obtained by the arrested relaxation method. The HF vibrational state distribution corresponding to the CH₃-group reaction is also compared to experimental data, and in both cases, $v = 2$ is the most populated level, but some discrepancy is observed for the $v = 1$ and 3 levels.

SUPPLEMENTARY MATERIAL

Codes (Ref. 37) and coefficients for PES evaluation.

ACKNOWLEDGMENTS

The authors thanked the National Research, Development and Innovation Office–NKFIH, Nos. K-125317 and K-146759, Project No. TKP2021-NVA-19, provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme, and the Momentum (Lendület) Program of the Hungarian Academy of Sciences for financial support. The authors also thanked Tibor Györi for his help with the PES development.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tímea Szűcs: Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (equal); Validation (equal); Visualization

(lead); Writing – original draft (lead); Writing – review & editing (equal). **Gábor Czako:** Conceptualization (lead); Formal analysis (supporting); Funding acquisition (lead); Investigation (supporting); Methodology (equal); Project administration (lead); Supervision (lead); Validation (equal); Writing – original draft (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹M. Qiu, Z. Ren, L. Che, D. Dai, S. A. Harich, X. Wang, X. Yang, C. Xu, D. Xie, M. Gustafsson, R. T. Skodje, Z. Sun, and D. H. Zhang, *Science* **311**, 1440 (2006).
- ²B. S. Agrawalla and D. W. Setser, *J. Phys. Chem.* **90**, 2450 (1986).
- ³M. A. Wickramaaratchi, D. W. Setser, H. Hildebrandt, B. Körbitzer, and H. Heydtmann, *Chem. Phys.* **94**, 109 (1985).
- ⁴A. M. Zolot and D. J. Nesbitt, *J. Chem. Phys.* **129**, 184305 (2008).
- ⁵J. J. Sloan, D. G. Watson, and J. Williamson, *Chem. Phys. Lett.* **74**, 481 (1980).
- ⁶C. Xiao, G. Shen, X. Wang, H. Fan, and X. Yang, *J. Phys. Chem. A* **114**, 4520 (2010).
- ⁷W. W. Harper, S. A. Nizkorodov, and D. J. Nesbitt, *J. Chem. Phys.* **113**, 3670 (2000).
- ⁸W. Zhang, H. Kawamata, and K. Liu, *Science* **325**, 303 (2009).
- ⁹E. S. Whitney, A. M. Zolot, A. B. McCoy, J. S. Francisco, and D. J. Nesbitt, *J. Chem. Phys.* **122**, 124310 (2005).
- ¹⁰R. G. Macdonald, J. J. Sloan, and P. T. Wassell, *Chem. Phys.* **41**, 201 (1979).
- ¹¹S. Wategaonkar and D. W. Setser, *J. Chem. Phys.* **86**, 4477 (1987).
- ¹²G. C. Schatz, J. M. Bowman, and A. Kuppermann, *J. Chem. Phys.* **63**, 674 (1975).
- ¹³Y. Ishikawa, T. Nakajima, T. Yanai, and K. Hirao, *Chem. Phys. Lett.* **363**, 458 (2002).
- ¹⁴J. Espinosa-García and M. Monge-Palacios, *J. Phys. Chem. A* **115**, 13759 (2011).
- ¹⁵L. Tian, Y. Zhu, H. Song, and M. Yang, *Phys. Chem. Chem. Phys.* **21**, 11385 (2019).
- ¹⁶J. P. Layfield, A. F. Sweeney, and D. Troya, *J. Phys. Chem. A* **113**, 4294 (2009).
- ¹⁷G. Czako, B. C. Shepler, B. J. Braams, and J. M. Bowman, *J. Chem. Phys.* **130**, 084301 (2009).
- ¹⁸D. Papp and G. Czako, *J. Chem. Phys.* **153**, 064305 (2020).
- ¹⁹H. Feng, W. Sun, Y. Xie, and H. F. Schaefer III, *Chem. Phys. Chem.* **14**, 896 (2013).
- ²⁰T. Szűcs and G. Czako, *J. Chem. Phys.* **159**, 134306 (2023).
- ²¹B. Fu, X. Shan, D. H. Zhang, and D. C. Clary, *Chem. Soc. Rev.* **46**, 7625 (2017).
- ²²T. Szűcs and G. Czako, *Phys. Chem. Chem. Phys.* **24**, 20249 (2022).
- ²³T. Györi and G. Czako, *J. Chem. Theory Comput.* **16**, 51 (2020).
- ²⁴D. Papp, V. Tajti, T. Györi, and G. Czako, *J. Phys. Chem. Lett.* **11**, 4762 (2020).
- ²⁵D. A. Tasi and G. Czako, *Chem. Sci.* **12**, 14369 (2021).
- ²⁶B. Gruber, V. Tajti, and G. Czako, *J. Chem. Phys.* **157**, 074307 (2022).
- ²⁷C. Yin, V. Tajti, and G. Czako, *Phys. Chem. Chem. Phys.* **24**, 24784 (2022).
- ²⁸A. B. Nacsas, V. Tajti, and G. Czako, *J. Chem. Phys.* **158**, 194306 (2023).
- ²⁹T. Györi and G. Czako, *J. Chem. Phys.* **156**, 071101 (2022).
- ³⁰W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Molecular Orbital Theory* (Wiley, New York, 1986).
- ³¹K. R. Shamasundar, G. Knizia, and H.-J. Werner, *J. Chem. Phys.* **135**, 054101 (2011).
- ³²G. Knizia, T. B. Adler, and H.-J. Werner, *J. Chem. Phys.* **130**, 054104 (2009).
- ³³T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ³⁴K. A. Peterson, T. B. Adler, and H.-J. Werner, *J. Chem. Phys.* **128**, 084102 (2008).

³⁵G. Knizia and H.-J. Werner, *J. Chem. Phys.* **128**, 154103 (2008).

³⁶H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, *MOLPRO, version 2015.1, a package of ab initio programs*, 2015, see <http://www.molpro.net>.

³⁷B. J. Braams and J. M. Bowman, *Int. Rev. Phys. Chem.* **28**, 577 (2009).

³⁸A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles, and P. Palmieri, *Mol. Phys.* **98**, 1823 (2000).

³⁹S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).

⁴⁰W. L. Hase, *Encyclopedia of Computational Chemistry* (Wiley, New York, 1998), pp. 399–407.