

Intermolecular Potential To Represent Collisions of Protonated Peptide Ions with Fluorinated Alkane Surfaces[†]

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The MP2/6-311++G(2df,2pd) level of theory was used to calculate intermolecular potential curves between CF₄, as a model for the C and F atoms of a fluorinated alkane surface, and CH₄, NH₃, NH₄⁺, H₂CO, and H₂O as models for different types of atoms and functional groups comprising protonated peptide ions. This level of theory was tested by comparisons with the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ theories. Explicit-atom (EA) analytic potential energy functions were then derived by fitting these potential energy curves with two-body potentials between the atoms of the two interacting molecules. An intermolecular potential for the interaction of a protonated peptide ion with a fluorinated alkane surface may be constructed from these two-body potentials. Intermolecular potentials, for which CF₄ is treated as a united atom (UA), were developed by isotropically averaging the CF₄ orientation for each of the EA potential energy curves. The intermolecular potential energy curves calculated for CF₄ are compared with curves calculated previously for CH₄ interacting with the same molecules, to consider the relative efficiency of energy transfer for protonated peptide ion collisions with hydrogenated and fluorinated alkane surfaces.

I. Introduction

Surface-induced dissociation (SID) is a mass spectrometry technique for fragmenting and analyzing ions by colliding them with surfaces.^{1–5} The specific fragments which are produced provide detailed information concerning the ion's structure and energetics for its fragmentation pathways. A particularly significant class of ions are protonated peptides, and understanding their properties is a critical component for the proteomics research field.⁶ SID is an important tool for studying these ions.^{2,5,7–15}

The efficiency of energy transfer to the ion during its collision with the surface depends on properties of both the ion and the surface. Classical trajectory simulations of SID^{16–22} have given an atomic-level understanding of the dynamics of the collisional energy transfer. Quantitative agreement is found between experimental energy-transfer efficiencies and those determined from the simulations.¹⁷ The simulations show that ions, including protonated peptide ions, may fragment by two mechanisms.^{17,19,22} One is a traditional RRKM mechanism²³ in which the collisionally excited ion first rebounds off the surface and then dissociates after intramolecular vibrational energy redistribution (IVR). The other is a shattering mechanism in which the ion dissociates as it collides with the surface.^{17,19,22} Recent experimental results for peptide ions are consistent with this shattering mechanism.¹⁵ The simulations of SID have investigated collisions of Cr⁺(CO)₆^{16,17,20} and protonated polyglycine and polyalanine ions^{18,19,21,22} [i.e. H⁺–(gly)_n and H⁺–(ala)_n, *n* = 1–5] with diamond {111} and hydrogenated alkanethiolate self-assembled monolayer (SAM) surfaces.

Different surfaces are used to fragment ions in SID experiments, and fluorinated hydrocarbon surfaces are found to be

particularly effective in transferring energy to the ion and inducing its dissociation.²⁴ In SID experiments of Cr⁺(CO)₆ with hydrogenated alkane SAM surfaces 11–12% of the collision energy is transferred to Cr⁺(CO)₆ internal energy,^{17,24} while in collisions with fluorinated SAMs this energy transfer is nearly a factor of 2 larger and 20%.²⁴ A similar difference in the efficiency of hydrogenated and fluorinated hydrocarbon surfaces to activate ions has been found in other experimental studies.^{3,8,14,25–28} The hydrogenated and fluorinated surfaces have been described as behaving like a “soft mattress” and a “hard wall”, respectively.²⁵ This difference has been ascribed to the projectile/target mass ratio and the rigidity of the fluorinated surface.²⁵

It is expected that computer simulations, of collisions of projectile ions with fluorinated surfaces, will be very useful for understanding why these surfaces energize projectiles more efficiently than do hydrogenated surfaces. However, to obtain accurate results from the simulations, it is important to have an accurate intermolecular potential for the interactions between the projectile ion and the surface, since the efficiency of energy transfer to the projectile's vibrational degrees of freedom depends on properties of this potential.²⁹ In the research reported here *ab initio* calculations are used to develop an empirical analytic intermolecular potential energy function for protonated peptide ions, containing H, C, N, and O atoms, colliding with fluorinated alkane surfaces. As was done in a previous study of protonated peptide ions colliding with hydrogenated surfaces,¹⁸ these *ab initio* calculations are performed for small molecules, which represent the atoms and functional groups of the peptides, interacting with CF₄, which represents the fluorine and carbon atoms of the fluorinated alkane surface.

II. Computational Procedure

Intermolecular potential energy curves were calculated between CF₄, as a model for the C and F atoms of a fluorinated

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TABLE 1: Comparison of *ab Initio* Intermolecular Potential Energies for $\text{CF}_4 + \text{NH}_3^a$

$R_{\text{C-N}}^b$	MP2 6-311++G(2df,2pd)	MP2 aug-cc-pVTZ	CCSD(T) aug-cc-pVTZ
1.0	1210.5	1205.4	1199.4
1.2	738.0	733.5	
1.4	459.3	455.3	
1.6	279.3	276.0	
1.8	161.4	158.8	
2.0	88.6	86.7	81.7
2.2	46.5	45.0	
2.4	23.3	22.1	
2.6	10.9	9.96	
2.8	4.57	3.81	
3.0	1.44	0.85	

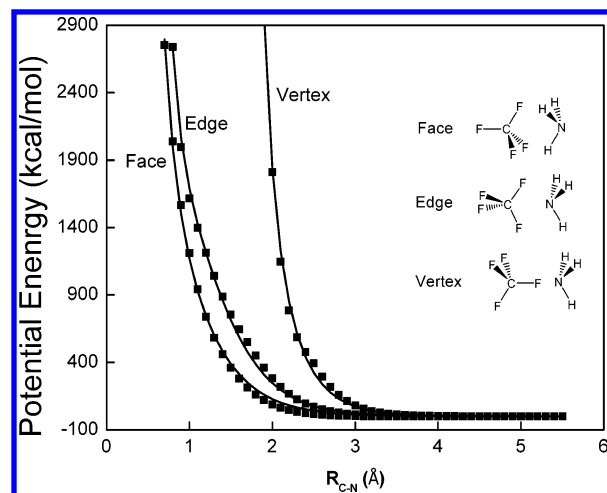
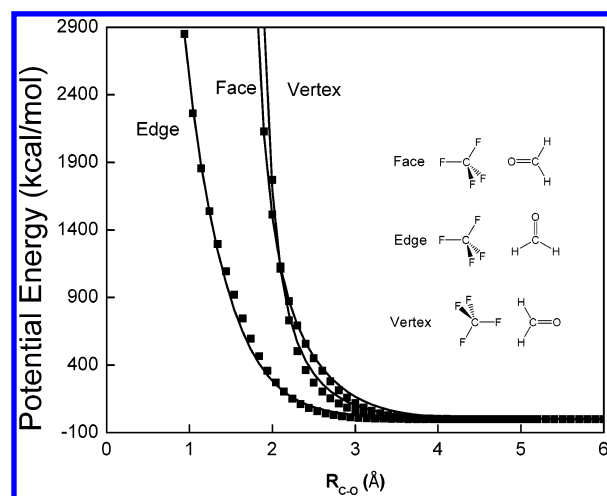
^a Energies are in kilocalories per mole and are calculated for the face potential curve in Figure 1. The MP2 energies include a BSSE correction,^{31–34} while the CCSD(T) energy does not. Related calculations indicate the BSSE correction for the CCSD(T) calculation should increase the energy by less than 5%. ^b The $R_{\text{C-N}}$ distance is in angstroms.

alkane surface, and CH_4 , NH_3 , NH_4^+ , H_2CO , and H_2O , as models for some of the different types of atoms and functional groups comprising protonated peptide ions. The *ab initio* calculations are carried out at the MP2 level of theory with the frozen-core approximation. The molecules are first optimized at the MP2 level of theory using as a single- ζ core and triple- ζ valence representation 6-311++G(2df,2pd) basis set, which includes a set of diffuse s- and p-type Gaussian functions on heavy atoms and three sets of d functions and one set of f functions for first-row atoms and two sets of p functions and one set of d functions for hydrogen atoms. The molecules were held fixed in these optimized geometries, and intermolecular potential energy curves were calculated for different orientations of the CF_4/CH_4 , CF_4/NH_3 , $\text{CF}_4/\text{NH}_4^+$, $\text{CF}_4/\text{H}_2\text{CO}$, and $\text{CF}_4/\text{H}_2\text{O}$ systems. Energies for these systems were calculated via the supermolecular approach³⁰ with the above basis set and full-counterpoise corrections.^{31–34} The MP2 *ab initio* calculations were carried out with the GAUSSIAN 98 suite of programs,³⁵ and the NWChem computer program³⁶ was used for the CCSD(T) calculations.

For SID experiments, in which peptide ions collide with surfaces, the collision energy is in the range of 10–100 eV.^{1–5} For this energy regime, the attractive part of the projectile/surface potential is unimportant and instead an accurate repulsive potential is necessary. In previous calculations of CH_4 interacting with CH_4 , NH_3 , NH_4^+ , H_2CO , and H_2O , the MP2/6-311++G(2df,2pd) level of theory used here gave accurate repulsive intermolecular potentials.¹⁸ To ensure that this level of theory is appropriate for the current study, intermolecular potential energies were also calculated for the CF_4/NH_3 system at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels of theory. The results are given in Table 1, and it is seen that the three theoretical methods give similar repulsive potentials. The two MP2 potential energy curves were scanned at a 0.1 Å interval, and the 6-311++G(2df,2pd) basis gives a potential energy minimum of -0.822 kcal/mol at $R_{\text{C-N}} = 3.7$ Å and the aug-cc-pVTZ basis gives a minimum of -1.05 kcal/mol at $R_{\text{C-N}} = 3.6$ Å.

III. Empirical Intermolecular Potentials

A. Explicit-Atom Models. *Ab initio* intermolecular potential energy curves were calculated for CF_4/NH_3 , CF_4/CH_4 , $\text{CF}_4/\text{NH}_4^+$, $\text{CF}_4/\text{H}_2\text{CO}$, and $\text{CF}_4/\text{H}_2\text{O}$, and those for CF_4/NH_3 and $\text{CF}_4/\text{H}_2\text{CO}$ are shown in Figures 1 and 2. Three potential curves were calculated for each of the systems by varying the

**Figure 1.** Fitted analytical potential energy function compared to the *ab initio* data (■) for the CF_4/NH_3 system.**Figure 2.** Same as Figure 1, but for the $\text{CF}_4/\text{H}_2\text{CO}$ system.

orientations of the two interacting molecules. The intermolecular potential curves between CF_4 and the other molecule are modeled by a sum of two-body potentials of the form

$$V_{xy} = A_{xy} \exp(-B_{xy} r_{xy}) + C_{xy}/r_{xy}^5 \quad (1)$$

where x corresponds to the C or F atom of CF_4 and y corresponds to the atom of the other molecule. Different exponents were considered for the last term in eq 1, and the value 5 was found to give the best overall representation of the potential energy curves.

The curves for the three orientations of a particular system were fit simultaneously by a sum of the two-body functions in eq 1, to derive explicit-atom (EA) intermolecular potentials. The fitting was accomplished by nonlinear least-squares, and excellent fits were obtained as illustrated by those for CF_4/NH_3 and $\text{CF}_4/\text{H}_2\text{CO}$ in Figures 1 and 2. The potential energy parameters derived from the fits, for all five of the systems, are listed in Table 2.

B. United-Atom Models. To simulate collisions of projectiles (particular large projectiles) with a surface, a model for the surface which has many atoms is often required. Simulations for such a large model may require a substantial amount of computer time, and, thus, there are incentives to develop approaches which reduce the size of the model. The number of atoms required to represent the surface may be reduced by treating the atoms within a functional group, e.g., CH_3 - or $-\text{CH}_2$ -,

TABLE 2: Parameters for the Explicit-Atom Two-Body Potential Energy Function in Equation 1

$x-y^a$	A_{xy}^b	B_{xy}^c	C_{xy}^d
CF₄/CH₄			
C–C	6500.0	6.7422	103.75
C–H	7514.6	5.1906	1.0937
F–C	13879.	3.0000	756.25
F–H	7132.7	5.1688	2.3438
CF₄/NH₃			
C–N	5348.2	4.0578	150.00
C–H	4249.8	2.4911	750.25
F–N	9250.0	3.0096	86.699
F–H	1200.2	7.8000	5.0000
CF₄/NH₄⁺			
C–N	7500.9	3.0208	23.379
C–H	11350.	5.2966	-0.10199
F–N	8441.8	3.2103	858.18
F–H	6206.7	4.9517	2.3576
CF₄/H₂CO^e			
C–C	5500.1	7.9000	690.42
C–O	20500.	4.7500	75.275
F–C	2500.0	2.1367	131.76
F–O	8000.0	2.8000	-50.000
CF₄/H₂O			
C–O	26112.	4.3075	13.574
C–H	714.15	5.8594	25.906
F–O	17248.	3.5536	58.257
F–H	5493.1	5.1927	159.65

^a x is an atom of the first molecule, CF₄, and y is an atom of the second molecule. ^b Units are kilocalories per mole. ^c Units are 1/Å. ^d Units are (kcal Å³)/mol. ^e C–H and F–H interactions are assumed to be the same as those for the CF₄/CH₄ system.

as a united atom (UA). Such potentials are widely used to represent surfaces,³⁷ interfaces,³⁸ and liquids.³⁹

UA potentials were developed for the -CF₃ and -CF₂- groups of a fluorinated alkane by assuming their potentials are the same as that for isotropic CF₄. To derive these UA potentials, potential curves for isotropic CF₄ were derived for the three EA curves calculated for each of the CF₄/NH₃, CF₄/CH₄, CF₄/NH₄⁺, CF₄/H₂CO, and CF₄/H₂O systems, e.g., Figures 1 and 2. To calculate a potential energy curve for an isotropic CF₄ interaction from the EA potentials, CF₄ is held rigid in its equilibrium geometry and then randomly rotated to calculate an average potential along each of the EA potential curves, e.g., the face potential energy curve in Figure 1 for which the CF₄⋯NH₃ separation is identified by R_{C-N} . This averaging is given by

$$V_R^{UA} = \frac{1}{N} \sum_{k=1}^N \sum_{i=1}^N \sum_{j=1}^N V_R(r_{ij}; \theta_k, \varphi_k, \chi_k) \quad (2)$$

where V_R^{UA} is the potential at separation R with the orientation of CF₄ isotropically averaged to represent a UA, N is the number of random orientations for the averaging, the i identify the C and F atoms of CF₄, the j identify the atoms of the molecule Y for which CF₄ is interacting, θ_k , φ_k , and χ_k are the randomly chosen Euler angles⁴⁰ for CF₄, and $V_R(r_{ij}; \theta_k, \varphi_k, \chi_k)$ is the two-body potential in eq 1 for the CF₄ random orientation and CF₄– Y separation R . Illustrative V_R^{UA} potential energy curves are plotted in Figures 3 and 4 for UA/NH₃ and UA/H₂CO.

To fit the V_R^{UA} potential energy curves, an analytic function is needed to represent the interaction between the CF₄ UA and the atoms of the Y molecule. This analytic function is modeled by a sum of two-body potentials between UA and the atoms of Y , e.g. the UA–N and the UA–H potentials for the UA/NH₃ system in Figure 3. A variety of two-body potential functions were tested, starting with eq 1, and it was found that the following function with both Buckingham and multiple r^n terms

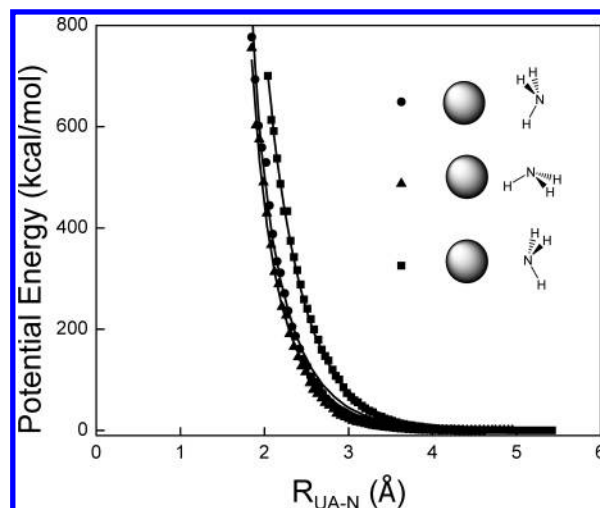


Figure 3. Potential energy curves for the CF₄/NH₃ system with CF₄ treated as a united atom (UA). The potential energy points for the ●, ■, and ▲ curves were calculated by averaging over random CF₄ orientations as described by eq 2. The solid lines are analytical fits to the points using the two-body potential in eq 3.

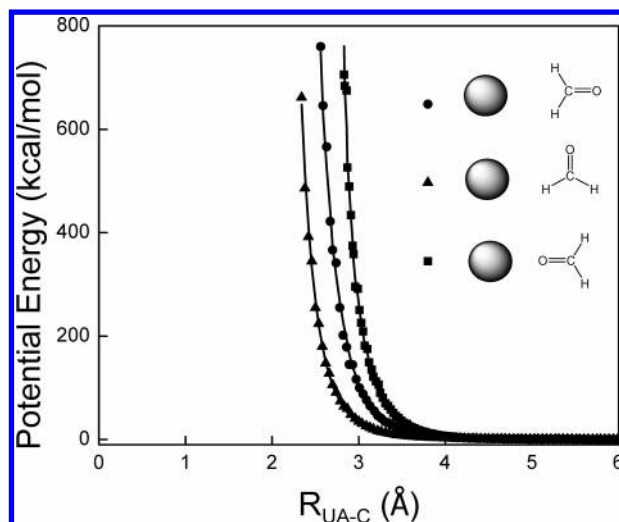


Figure 4. Same as Figure 3, but for the CF₄/H₂CO system.

was required to achieve an acceptable fit to the potential energy points; i.e.,

$$V_{UA,y} = A_y \exp(-B_y r) + C_y/r^n + D_y/r^{12} + E_y/r^6 \quad (3)$$

where r is the distance between the C atom of CF₄ (i.e., the center of UA) and the y atom of Y . The three UA potential energy curves of a particular system were fit simultaneously by a sum of the two-body functions in eq 3 using nonlinear least-squares. The potential energy parameters derived from the fits are listed in Table 3.

Excellent fits to the UA V_R^{UA} potential energy curves were obtained and those for UA/NH₃ and UA/H₂CO are given by the solid lines in Figures 3 and 4. It was not possible to obtain good fits using eq 3, for energies higher than approximately 700 kcal/mol, so the fits are restricted to energies lower than this value. However, these UA potentials should be applicable to SID experiments with collision energies much higher than 700 kcal/mol (i.e., ~30 eV), since the collision between a protonated peptide and fluorinated alkane is expected to be distributed between multiple -CF₃ and -CF₂- groups. This will certainly be the case for very large peptides, for which large models for the surface will be required. The UA model will be particularly beneficial for these systems.

TABLE 3: Parameters for the United-Atom Two-Body Potential Energy Function in Equation 3

y^a	A_y^b	B_y^c	C_y^d	n_y	D_y^e	E_y^f
UA/CH ₄						
C	136720	2.4584	946.80	9	2312500	-18937
H	27730	1.9905	999.79	6	30024	-11.691
UA/NH ₃						
N	22573	2.2275	121.92	7	461550	-1019.8
H	9499.4	2.4806	848.85	6	25049	-49.634
UA/NH ₄ ⁺						
N	94718	2.6844	998.98	5	1504800	-350.05
H	36125	3.3496	153.45	5	11937	-49.999
UA/CH ₂ O						
C	11323	2.4850	901.92	8	2494400	-10091
O	18708	2.2434	165.27	9	250190	-2080.8
H	34043	2.9916	890.57	6	259990	-64.449
UA/H ₂ O						
O	21965	2.3266	987.92	6	437510	-230.96
H	17797	2.4998	232.55	8	39991	-687.27

^a y is an atom of the molecule with which the CF₄ UA atom interacts.

^b Units are kilocalories per mole. ^c Units are 1/Å. ^d Units are (kcal Å³)/mol. ^e Units are (kcal Å¹²)/mol. ^f Units are in (kcal Å⁶)/mol.

IV. Comparison of CF₄ and CH₄ Intermolecular Potentials

As discussed in the Introduction, when a projectile collides with a fluorinated alkane surface more of the collision energy is transferred to the vibrational energy of the projectile than when it collides with a hydrogenated surface. One of the properties which affects the efficiency of translation to vibration (T→V) energy transfer is the range parameter L for the interaction potential $V(r)$ between the collision partners;^{41–43} i.e.,

$$V(r) = V_0 \exp(-r/L) \quad (4)$$

An increase in L may move the collision from the sudden limit, for which T→V is efficient, to inefficient energy transfer in the adiabatic limit.

In previous work,¹⁸ intermolecular potentials were calculated between CH₄, as a model for hydrogenated alkanes, and CH₄, NH₃, NH₄⁺, H₂CO, and H₂O, as models for atoms and functional groups of protonated peptides. It is of interest to compare these potentials with those calculated here between CF₄, as a model for a fluorinated alkane, and the same group of five molecules. A comparison of the intermolecular potentials for CH₄ and CF₄, interacting with a specific molecule, shows that for each molecule the potentials with CF₄ are longer range and more repulsive and have larger values of L than those for CH₄. To illustrate this difference in the CH₄ and CF₄ intermolecular potentials, the face, edge, and vertex potentials for CH₄/NH₄⁺ and CF₄/NH₄⁺ are compared in Figure 5. The former potentials were presented previously in Figure 3 of ref 18. The relative orientation of the two interacting molecules, for the edge potential curve, is that used previously in ref 18. The larger range parameters for CF₄ as compared to CH₄, suggests that fluorinated alkane surfaces will adsorb the peptide's collision energy less efficiently than does the hydrogenated surface and, thus, more energy should be available for transfer to peptide vibration for collision with the fluorinated surface.

V. Summary

In the research presented here ab initio calculations were used to derive both explicit-atom (EA) and united-atom (UA) empirical analytic potential energy functions which may be used in chemical dynamics simulations of collisions of protonated

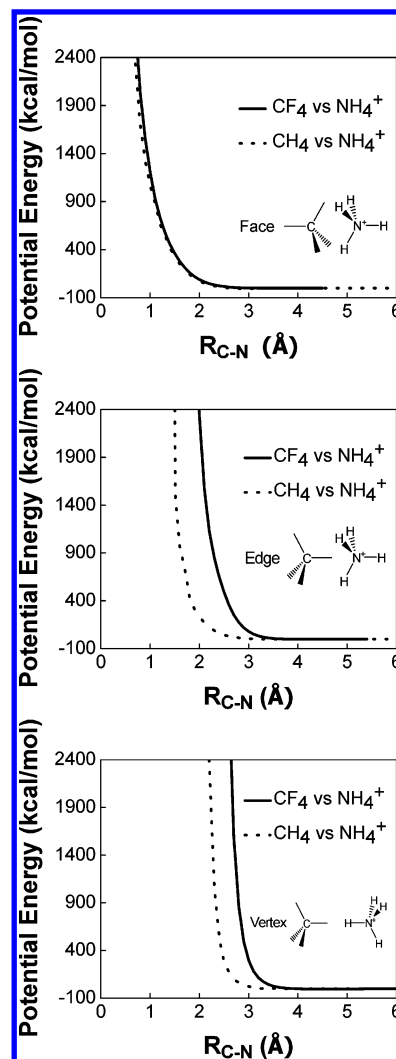


Figure 5. Comparison of face, edge, and vertex EA intermolecular potential energy curves for CF₄/NH₄⁺ and CH₄/NH₄⁺.

peptide ions with fluorinated alkane surfaces. These functions represent collisions with energies of 100 eV and higher. The MP2/6-311++G(2df,2pd) theory was used for the ab initio calculations, and it was tested by comparisons with energies determined with the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ theories. The EA potential energy function was “built” by fitting a sum of two-body functions to intermolecular potentials between CF₄, as a model for the C and F atoms of a fluorinated alkane surface, and CH₄, NH₃, NH₄⁺, H₂CO, and H₂O, as models for different types of atoms and functional groups comprising protonated peptide ions. To illustrate, the CF₄–NH₃ intermolecular potential is written as a sum of C–N, C–H, F–N, and F–H two-body potential functions. These two-body functions and those for the other CF₄ molecule potentials may be used to construct the intermolecular potential for the collision of a protonated peptide ion with a fluorinated alkane surface.

To decrease the number of potential energy terms required to represent the collision between the protonated peptide and the fluorinated surface, and thus decrease the amount of computational time required for a chemical dynamics simulation of the collision, a UA model was developed for the CF₃ and CF₂ groups of the fluorinated alkane. This was done by treating CF₄ as a UA and isotropically averaging the CF₄ orientation for each of the EA potential energy curves. UA parameters for CF₄ were then derived by fitting these isotropically averaged

potentials. This UA intermolecular potential model is expected to be particularly useful for chemical dynamics simulations of collisions of large protonated peptide ions.

In previous work,¹⁸ the above approach was used to derive an intermolecular potential for protonated peptide ions colliding with hydrogenated alkane surfaces, by calculating potential energy curves for CH₄ interacting with representative molecules. The results of this study and those of the study presented here were used to compare the ab initio intermolecular potential energy curves for CH₄ and CF₄, e.g., CH₄–NH₃ and CF₄–NH₃. The latter are substantially longer range and more repulsive, which indicates that, for the same peptide ion collision energy, less energy should be transferred to the fluorinated surface as compared to the hydrogenated surface. This suggestion is in agreement with experimental results.^{3,8,14,24–28} However, properties of the surface may also be an important factor in describing the energy transfer¹⁷ and chemical dynamics simulations, which include the effects of both the peptide-H⁺/surface intermolecular potential and the surface intramolecular potential, are needed⁴⁴ to obtain a clear understanding of the origin(s) of the different energy-transfer efficiencies for fluorinated and hydrogenated surfaces.

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