Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for
EVB and polarizable MM study of energy relaxation in fluorine-acetonitrile reactions

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1. Covalent-Ionic Model of DF molecule

1.1. MRCI Calculation

CASSCF/MRCI-F12[1] calculations were performed for isolated HF molecule with all the valence orbitals (H 1s orbital, F 2s and 2p orbitals) in the active space and the F 1s orbital in the inactive space. The CI energies were further corrected by the Davidson correction method. The dipole moment at a given geometry was calculated by the finite difference approximation method as the energy derivative,

$$\mu \cong \frac{E(d) - E(-d)}{2d}$$

in which, d is the strength of the external dipole field added to the one-electron Hamiltonian. The direction of the field is oriented along the D-F bond axis. The calculated energy and dipole moment as a function of HF interatomic distance is presented in Figure S1.

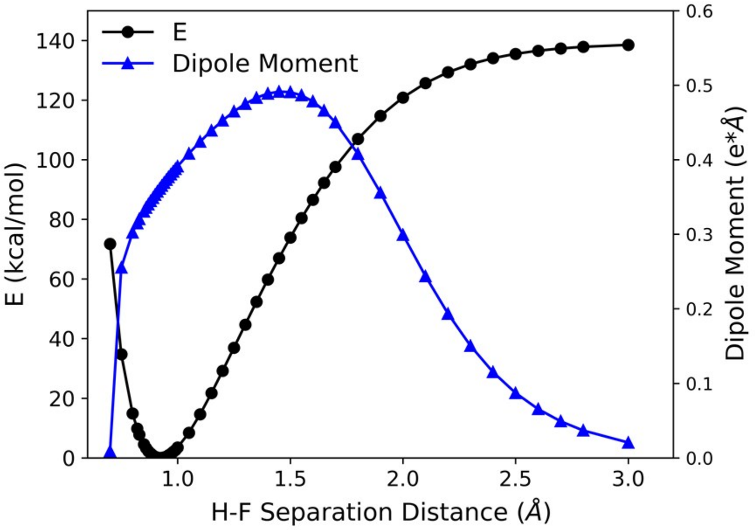

Figure S1. Energy (kcal/mol) and dipole moments (e*Å) along the H-F stretch coordinate at the MRCI-F12/aug-cc-pVTZ level.

1.2. Ab initio Valence Bond Calculations

The ab initio valence bond (VB) calculations, mainly localized VBSCF and VBCISD with strictly localized VB occupied and virtual orbitals for the covalent D-F and ionic $D^+ F^-$ states, were performed using the XMVB software package.[2] The basis set used is 6-311+G**. Conceptually, the basis functions are divided into four blocks, including σ-type (s, pz, dxx, dyy and dzz) basis functions centered on F, px and dxz type basis functions centered on F, py and dyz type basis functions centered on F, and σ-type (s and pz) basis functions centered on D. The occupied VB orbitals within a specific block are constructed using only the basis functions belonging to that block. In the CI-calculation, excited VB structures are constructed by replacing occupied orbitals with virtual orbitals within the same block. The F 1s orbital was chosen to be frozen in the CI-type VB calculation.

Table S1. Comparison of the $IP(H) + EA(F)$ value (kcal/mol) predicted by different *ab initio* VB methods and experiment.

$IP(H) + EA(F)$	6-31+G*	6-31+G**	6-31++G**	6-311+G**
VBSCF	281.13	281.13	281.48	282.65
VBCISD	232.60	232.60	232.96	238.90
Exp.	235.32			

1.3. Covalent-Ionic DF EVB Model Fitting

The procedure shown in Figure S2 was followed to fit the covalent-ionic EVB model of the DF molecule. As described in the main context, the covalent state is fitted by a generalized Morse function, while the ionic state is described by a modified electrostatic potential. The general expression used for H_{12} is shown as follows:

$$H_{12} = \sum_{i=1}^{3} A_i * exp\left\{ -\frac{1}{2}\left(\frac{(r - C_i)}{\sigma_i}\right)^2 \right\}$$

in which, A_i, C_i and σ_i correspond to the amplitude, center and width of the i th Gaussian function. In the fitting, several parameters in the diagonal and off-diagonal matrix element expressions are varied in order to reproduce as accurately as possible both the MRCI-F12 energies and dipole moments. The final parameters are listed in Table S2.

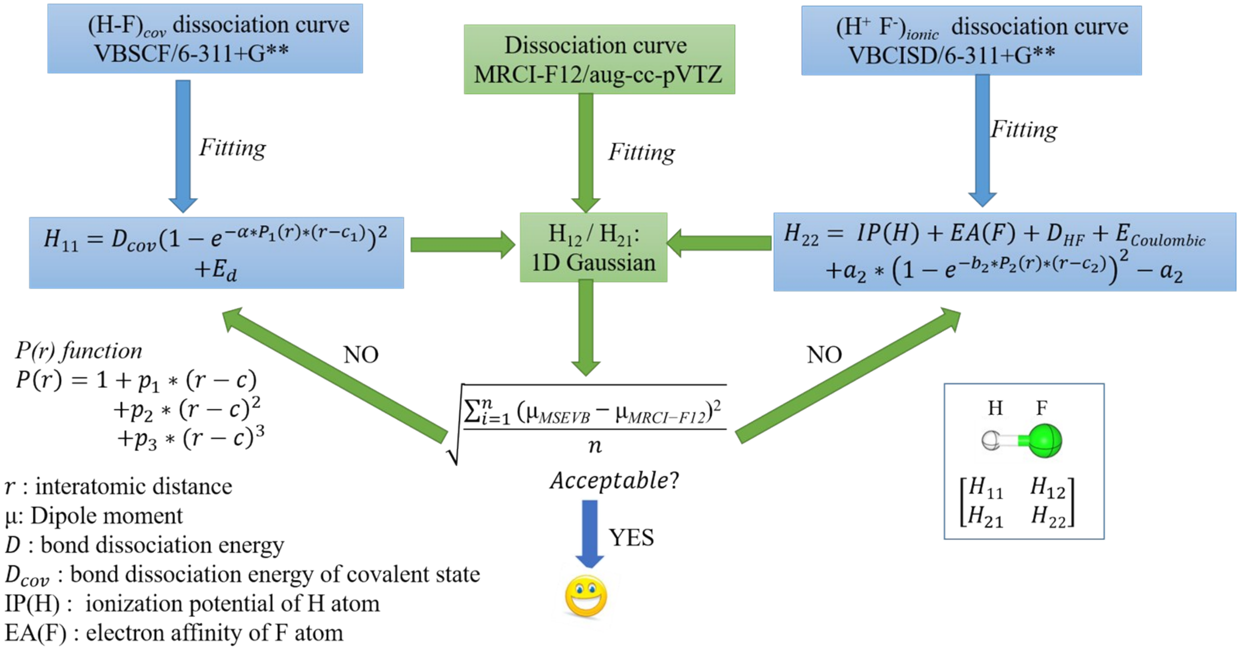

Figure S2. The work flow to fit the covalent-ionic EVB model of HF molecule.

Table S2. Determined parameters in the covalent-ionic EVB model.

H_{11} elements		H_{22} elements		H_{12} elements	
D_{cov}	56.26	D_e	139.76	A_1	109.77
c_1	0.8663	a_2	3.4908	C_1	0.95
α_1	3.9771	b_2	4.6493	σ_1	0.47
p_1	0.1394	c_2	2.7335	A_2	-27.04
p_2	-0.7260	p_4	1.1947	C_2	0.61
p_3	0.3780	p_5	0.5800	σ_2	0.05
E_d	83.50	p_6	0.0863	A_3	33.58
				C_3	1.77
				σ_3	0.34

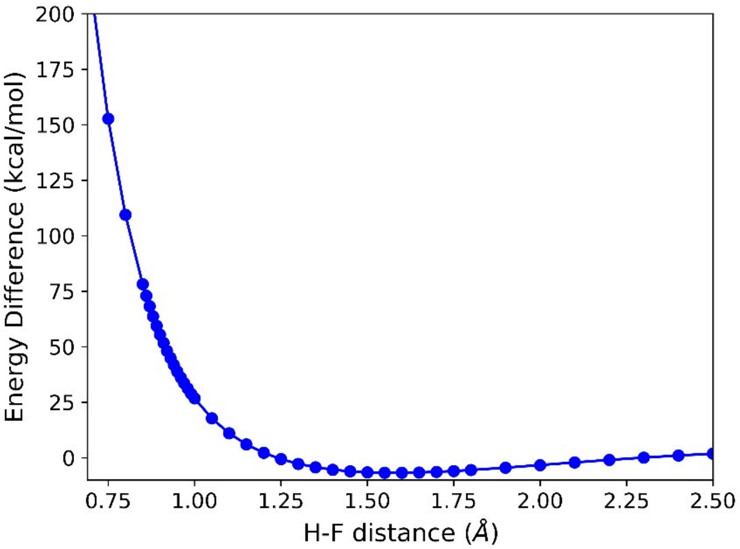

Figure S3. Difference in energy (kcal/mol) between the potential energy curve for the ionic state as obtained from VBCISD calculations, and from the buffered coulombic expression in MMFF. For all distances above 1.25 Å, the two expressions agree well.

The non-bonded parameters for the atoms in the covalent DF state can be found below in Tinker MMFF format. Including a positive charge on the D^+ centre in the ionic state was accomplished in Tinker through by some coding work (kcharge.f), while the non-bond parameter of F^- used the original value.

```
atom        56   11    F     "FLUORINE"                   9    18.998    1
atom       217  102    D   "D in covalent DF state"       1     2.016    1
mmffvdw     11     1.07111          1.28124    8.71732    3.83487     A
mmffvdw      102   0.00003          0.49438     0.02068    1.91530     D
mmffbci      11    102      0.0000     0
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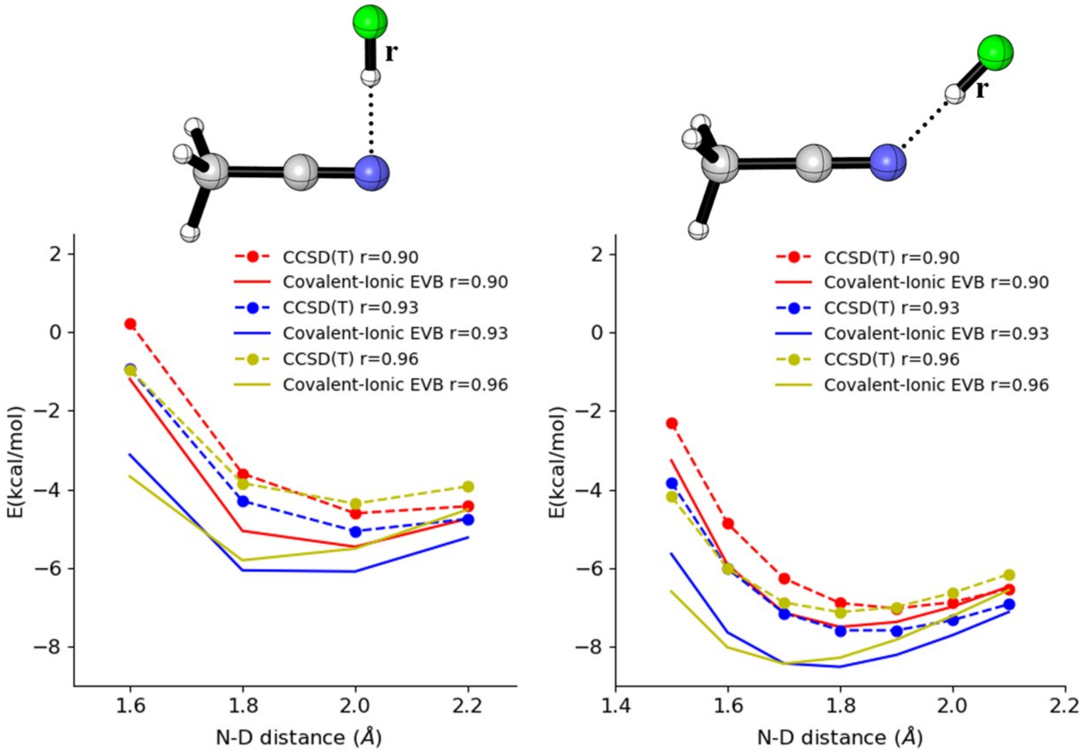

Figure S4. Energies (kcal/mol) of the CD_3CN---DF complex for bent structures (angle C-N-D of respectively 90 and 135 degrees) around the potential energy surface minimum, as obtained by CCSD(T)-F12 and covalent-ionic EVB methods.

This new EVB model could roughly reproduce the CCSD(T)-F12 energy curve for CD_3CN---DF complex in bent form, though the energies are underestimated by ~2 kcal/mol when the N-D distance becomes smaller (<1.8 Å).

2. Proton-Transfer EVB Model

In accordance with previous work,[3] the force constants of the C-D stretch and C≡N stretch in CD_3CN were modified to give frequencies in agreement with experiment. The D-F bond was described by the standard Morse potential, and partial charges on D and F atom were set as ±0.414. The vdW parameter of D was chosen as the same as that of the hydrogen atom in water in the MMFF. In the proton transfer state, bonded parameters involving the D-N bond and vdW parameters of the D and N atoms were modified to be identical with those in isocyanide. The partial charges for the D, N and C (bonded with N) atoms were specified as 0.323, 0.612 and 0.200, respectively. The overall charge in the methyl group thereby turns out to be -0.135. All other parameters used original values in MMFF. The periodic box was constructed with size of 17.8 × 17.8 × 17.8 Å^3, containing 1 CD_2CN, 1 DF and 61 CD_3CN molecules, resulting into a 64 × 64 EVB matrix. The solvation system firstly underwent pre-equilibration NVT simulation of 100 ps, followed by the non-equilibrium vibrational relaxation dynamics. The van der Waals interaction calculation applied an 8.5 Å cutoff switching from 6.5 Å.

3. AMOEBA Force Field

The AMOEBA force field parameters for deuterium fluoride are displayed below in Tinker AMOEBA format. The atomic multipole parameter of DF was obtained by strictly following the seven-step protocol as addressed in the original AMOEBA paper.[4,5] GDMA of version 2[6] was utilized to generate the initial atomic multipoles in the global frame based on the electron density matrix at the MP2/6-311G(1d,1p) level. The sub-program POLEDIT of the Tinker package was then applied to convert the multipole values to the TINKER permanent multipoles, and the subprogram POTENTIAL was used to fit the multipoles to the electrostatic potential at the MP2/aug-cc-pVTZ level. The polarizability of the D and F atoms uses the suggested values in AMOEBA, i.e, 0.6 for F element and 0.496 for D element. The vdW parameters were obtained by fitting to the $CD_3CN\cdots DF$ post-product potential energy surface.

```
atom      352  103   F      "F in deuterium fluoride "          9    18.998    1
atom      353  104   D      "D in deuterium fluoride "          1     2.016    1
bond      103  104   694.978     0.917
```

```
vdw        103   4.84212499399     0.0503967839474
vdw        104   2.90665504304     0.00328415898447     0.910
multipole   352  353               -0.36530
                                    0.00000    0.00000    0.29455
                                   -0.31110
                                    0.00000   -0.31110
                                    0.00000    0.00000    0.62220
multipole   353  352                0.36530
                                    0.00000    0.00000   -0.19110
                                   -0.12867
                                    0.00000   -0.12867
                                    0.00000    0.00000    0.25734
polarize     352         0.6000    0.3900     353
polarize     353         0.4960    0.3900     352
```

In terms of the AMOEBA force field for CD_3CN molecule, some modifications were made on the bond parameters so as to better reproduce experimental vibrational frequencies (Table S3).[7] The bond stretch, angle bending, stretch-bending and torsion parameters involved in CD_3CN are listed below:

```
atom       210   79    C     "Acetonitrile CN"           6    12.011    2
atom       211   80    N     "Acetonitrile CN"           7    14.007    1
atom       212   82    C     "Acetonitrile CD3"          6    12.011    4
atom       213   83    D     "Acetonitrile D3C"          1     2.016    1
bond        79   80        1280.0   1.1600
bond        79   81         462.00  1.0650
bond        79   82         380.00  1.4570
bond        82   83         356.60  1.0930
angle      80   79   82      10.00     180.00
angle      79   82   83      45.00     109.92
angle      83   82   83      40.00     109.02
strbnd      80   79   82      9.00       9.00
strbnd      79   82   83     11.50      11.50
torsion     80   79   82   83      0.000 0.0 1   0.000 180.0 2   0.000 0.0 3
```

Table S3. Frequency (cm^{-1}) of CD_3CN obtained by AMOEBA force field compared with experimental frequency.

	AMOEBA Frequency	*Experimental Frequency*
CD_3CN	*367*	*331*
	367	
	785	*831*
	802	*847*
	802	
	1054	*1046*
	1054	*1046*
	1196	*1110*
	2123	*2126*
	2275	*2257*
	2275	
	2290	*2278*

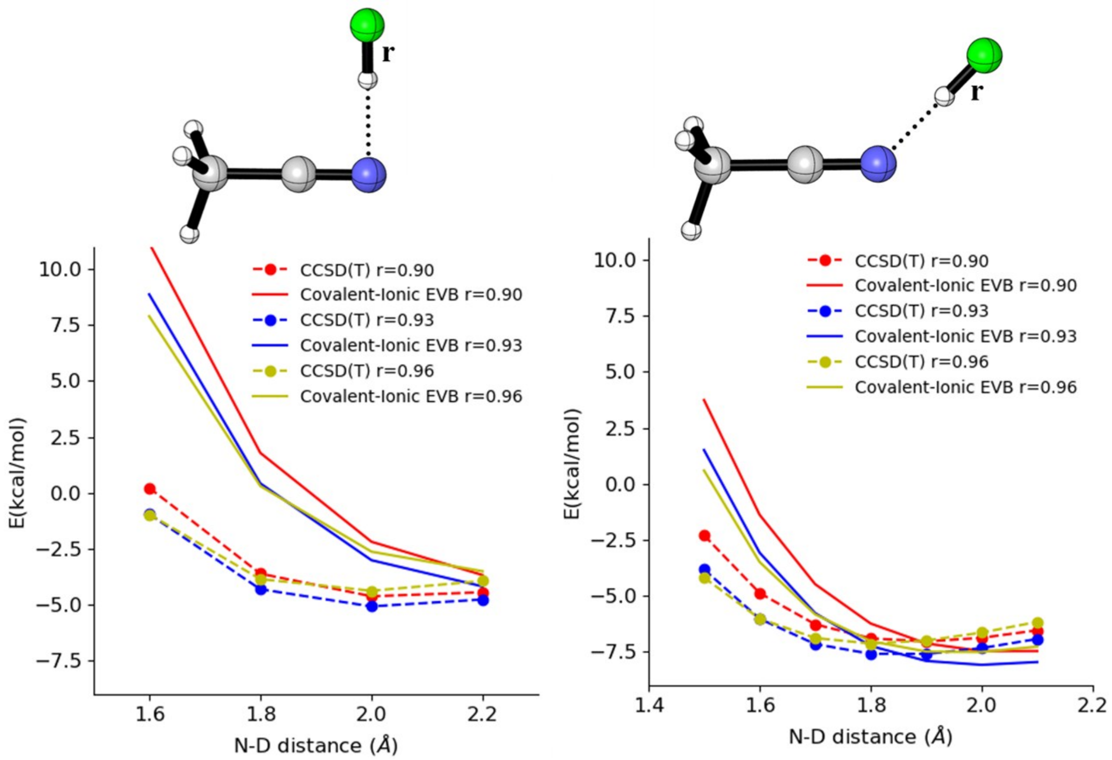

Figure S5. Energies (kcal/mol) of the CD_3CN---DF complex for bent structures (angle C-N-D of respectively 90 and 135 degrees) around the potential energy surface minimum, as described by CCSD(T)-F12 and AMOEBA methods.

The current AMOEBA model gives very large energy for those non-linear complexes, especially at the short N-D distance. Note that those conformations are in fact higher in energy than the linear minimum conformations with identical N-D and D-F distances, and therefore they are less populated in the dynamics. Of course, the current AMOEBA model is not perfect and may suffer from conformational sampling problem, but we believe that it has captured most of phenomena in energy relaxation based on the reproduced energy relaxation time-scale, and similar C_a-N_b radial distribution compared with proton transfer EVB model.

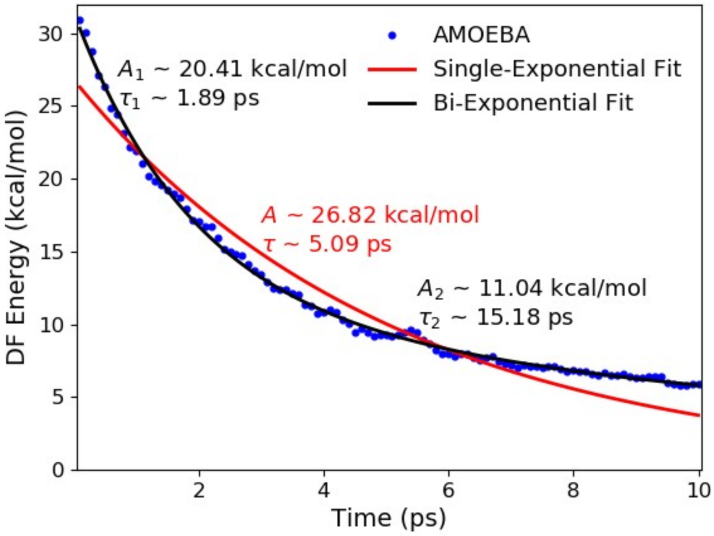

Figure S6. Energy relaxation profile of vibrationally excited DF in NEVRD simulation obtained by using the AMOEBA force field. Fitting to a single exponential decay function (red curve) is far from satisfactory, and fitting to a bi-exponential function (black curve) could well describe the energy relaxation.

4. Radial Distribution Function

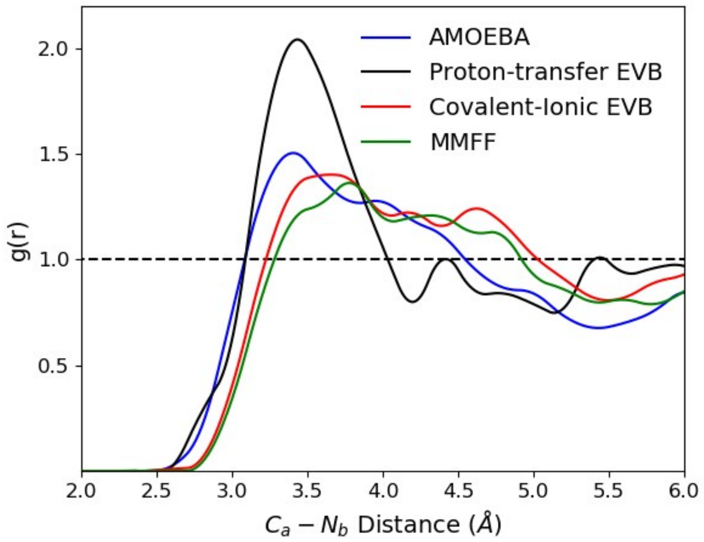

Figure S7. Radial distribution function g(r) of C_a and N_b in the 1 ps relaxation dynamics trajectories of vibrationally excited DF (~35 kcal/mol) in solution predicted by different models. C_a denotes the sp-hybridized C of the H-bonded solvent, and N_b corresponds to the N atom of the next-nearest solvent molecule.

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