

Compound-Model Morphed Potential for the Hydrogen Bond HCN–HF

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Motivation

- The importance and ubiquity of the hydrogen bond in Chemistry and Biology make it desirable to characterize and understand this non-covalent interaction as completely as possible.
- The morphing method relies on an appropriate combination of experimental and *ab initio*-calculated properties.
- HCN-HF is a highly suitable prototype of a simple hydrogen-bonded complex to morph a detailed potential energy surface and test its accuracy/predictive ability.

Motivation

- R. K. Thomas demonstrated in 1971 that the infrared spectrum of HCN-HF can be observed in an equilibrium gas mixture of HCN and HF, even at room temperature, by using a long path cell.
 - R. K. Thomas, Proc. R. Soc. Lond. A, 325 (1971) 133.
- Bevan and co-workers resolved vibration-rotation structure in many infrared bands of HCN-HF in equilibrium gas mixtures of HCN and HF by using very low gas pressures in combination with cell path lengths of 96 m.
 - (fundamentals, overtones, hot bands, sum and difference bands)

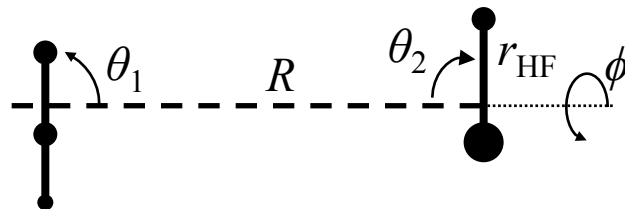
Motivation

Example of important results from Bevan's studies include:

- Pre-dissociation lifetimes
 - D. Bender, M. Eliades, D. A. Danzeiser, M. W. Jackson, J. W. Bevan, J. Chem. Phys. 86 (1987) 1225.
- The dissociation energy D_e
 - B. A. Wofford, M. E. Eliades, S. G. Lieb, J. W. Bevan, J. Chem. Phys. 87 (1987) 5674.
- Force fields
 - B. A. Wofford, S. G. Lieb, J. W. Bevan, J. Chem. Phys. 87 (1987) 4478.

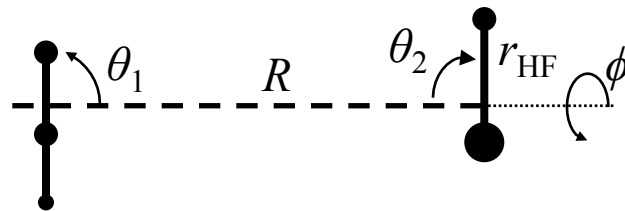
5-D *Ab Initio* Calculations

- CCSD(T)/aug-cc-pVTZ (BSSE corrected)
- CCSD(T)/aug-cc-pVTZ (Not BSSE corrected)
- MP2/aug-cc-pVTZ (BSSE corrected)
- MP2/aug-cc-pVQZ (BSSE corrected)



5-D *Ab Initio* Calculations

- 16 R points from 2.85 to 9.00 Å
- 13 r_{HF} points from 0.66 to 1.63 Å
- HCN molecule is frozen
 - H-C distance 1.064 Å
 - C-N distance 1.1564 Å
- 636 angular points (θ_1, θ_2, ϕ)
- 132,288 total points



Interpolation of the *Ab Initio* PES

- The full 5-D potential for HCN-HF system is given by

$$V(R, r, \theta_1, \theta_2, \phi) = V^{\text{int}}(R, r, \theta_1, \theta_2, \phi) + V_{\text{HF}}(r)$$

RKR potential

- Angular coordinates $(\theta_1, \theta_2, \phi)$: IMLS

$$V_A^{\text{int}}(R_i, r_j, \theta_1, \theta_2, \phi) = \sum_{\Lambda} v_{\Lambda, i, j}(\theta_1, \theta_2, \phi) A_{\Lambda}(\theta_1, \theta_2, \phi)$$

expansion coefficients

Expansion in associated Legendre polynomials

J. Castillo-Chará, J. W. Bevan, R. R. Lucchese,
Comput. Phys. Commun. 145 (2002) 48.

Interpolation of the *Ab Initio* PES

- Radial potential is obtained by interpolating the angular potential on the grid of R_i points, at each value of r_j at fixed angular coordinates.

$$V_{\Omega}^{\text{int}}(R, r_j, \theta_1, \theta_2, \phi)$$

expansion coefficients

$$= (|V_{\text{min}}| + V_{\text{M}}) \left[\exp \left(\sum_i \alpha_{i,j}(\theta_1, \theta_2, \phi) q_1^{2,3}(R_i, R) \right) - 1 \right]$$

300 cm⁻¹

- Reproducing Kernel Hilbert Space (RKHS)
- T.-S. Ho, H. Rabitz, J. Chem. Phys. 104 (1996) 2584.

Interpolation of the *Ab Initio* PES

- At each value of the 4-D grid $(R, \theta_1, \theta_2, \phi)$, the final interpolated potential is then given by

expansion coefficients

$$V^{\text{int}}(R, r, \theta_1, \theta_2, \phi) = \sum_j C_j(R, \theta_1, \theta_2, \phi) \bar{q}_{2,j}^2 \left(\frac{(r - r_{\text{start}})}{(r_{\text{end}} - r_{\text{start}})} \right)$$

- Reproducing Kernel Hilbert Space (RKHS)
- T.-S. Ho, H. Rabitz, J. Chem. Phys. 104 (1996) 2584.

Morphing the PES

- Hamiltonian (vibrational adiabatic approximation)

$$H = T_1 + T_2 + \frac{1}{2\mu_{1,2}R^2} \left[-\hbar^2 \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + J^2 + j_{1,2}^2 - 2\mathbf{j}_{1,2} \cdot \mathbf{J} \right] + V^v(R, \theta_1, \theta_2, \phi)$$

- CMM-RC

$$V_{\text{CMM-RC}}(R) = C_1 [V_{\text{MP2}}(R')]_{\text{QZ}}^{\text{CP}} + C_2 \left\{ [V_{\text{CCSD(T)}}(R')]_{\text{TZ}}^{\text{CP}} - [V_{\text{CCSD(T)}}(R')]_{\text{TZ}}^{\text{NO CP}} \right\} + C_3 \left\{ [V_{\text{CCSD(T)}}(R')]_{\text{TZ}}^{\text{CP}} - [V_{\text{MP2}}(R')]_{\text{TZ}}^{\text{CP}} \right\}$$

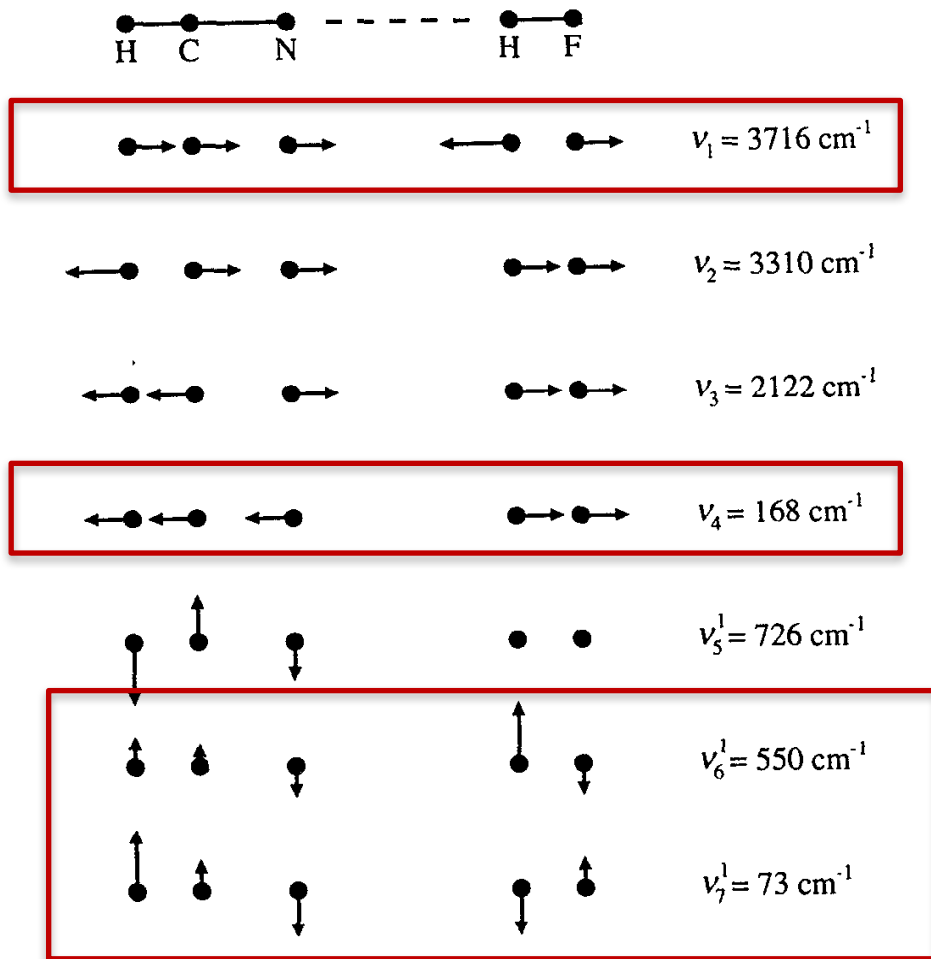
$$R' = C_4 (R - R_f) + (1.0 + C_5) R_f$$

Corrects for BSSE

Corrects for correlation energy

Initial Values: $C_1 = 1.0$, $C_2 = 0.0$, $C_3 = 1.0$, $C_4 = 1.0$, and $C_5 = 0.0$

Normal Modes vibration of HCN-HF



A. Quiñones, G. Bandarage, J. W. Bevan, R. R. Lucchese,
 J. Chem. Phys. 97 (1992) 2209.

Morphed 5-D PES for HCN-HF

Observable (cm ⁻¹)	$V_{\text{CMM-RC}}^{(0)}$	$V_{\text{CMM-RC}}^{(5)}$	Exp
$B(\text{GS}) \times 10^{-2}$	11.877	11.975	11.9788043(7)
$D(\text{GS}) \times 10^{-8}$	24.1	23.6	23.32(7)
$B(\nu_1) \times 10^{-2}$	12.108	12.200	12.20953(10)
$D(\nu_1) \times 10^{-8}$	21.7	21.6	28.54(12)
$B(\nu_4) \times 10^{-2}$	11.708	11.786	11.77252(31)
$D(\nu_4) \times 10^{-8}$	11.7	13.9	18.88(27)
$B(\nu_6^1) \times 10^{-2}$	11.667	11.765	11.76529(10)
$D(\nu_6^1) \times 10^{-8}$	27.5	27.2	27.91(5)
$B(\nu_7^1) \times 10^{-2}$	11.991	12.085	12.0840(1)
$D(\nu_7^1) \times 10^{-8}$	24.5	23.8	26.43(4)

Morphed 5-D PES for HCN-HF

Observable (cm ⁻¹)	$V_{\text{CMM-RC}}^{(0)}$	$V_{\text{CMM-RC}}^{(5)}$	Exp
D_0	1922	1969	1970(10)
ν_1	3721.96	3716.21	3716.2116(20)
ν_4	165.42	168.34	168.344(21)
ν_6^1	541.72	550.02	550.0285(2)
ν_7^1	72.72	73.60	73.5831(5)
RMS	273.1	1.7	

Band origin fundamental vibrational frequencies in HCN-HF were fitted to an average absolute error of 0.01 cm⁻¹.

Optimized values for the morphing parameters for HCN-HF

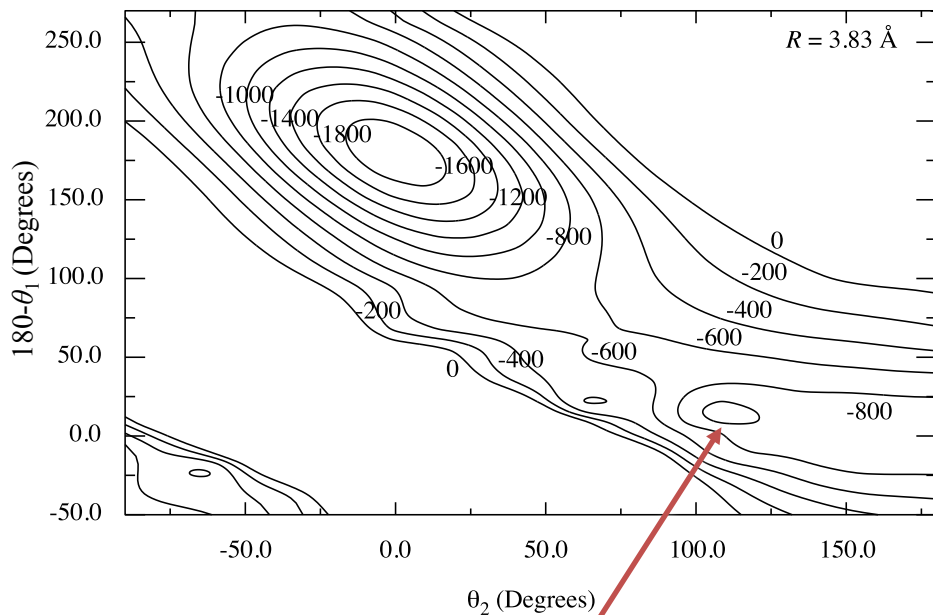
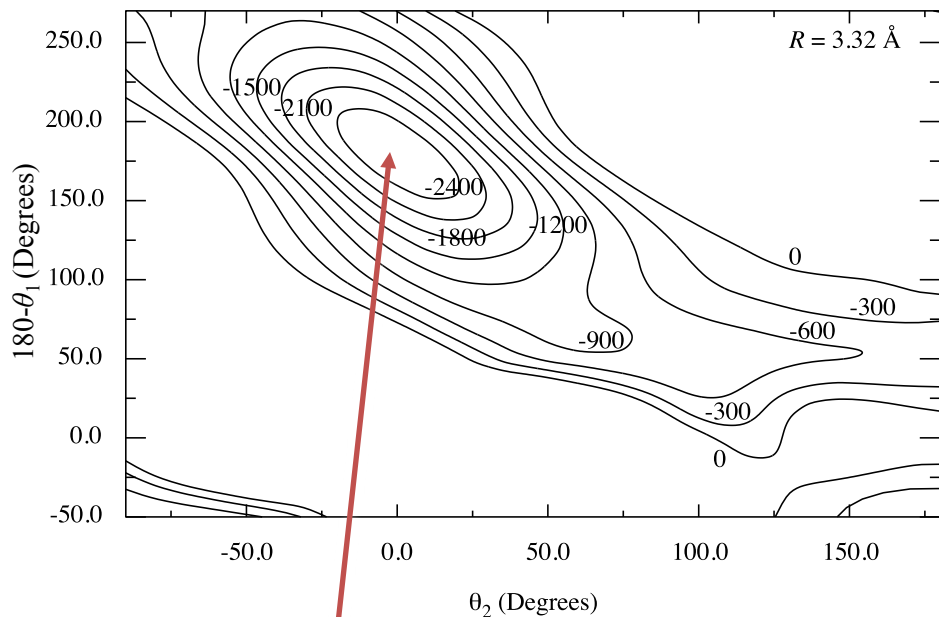
α	$C_{\alpha}^{(0)}$	$V_{\text{CMM-RC}}^{(5)}$
1	1.0	1.0940(14)
2	0.0	0.848(19)
3	1.0	1.3151(54)
4	1.0	0.99305(15)
5	0.0	0.00849(11)

Most of the corrections to the unmorphed potential are for the BSSE (C_2 coefficient) and for the correlation energy (C_3 coefficient).

It is found that the counterpoise method under corrected the BSSE by 85(2)%.

The CMM-RC potential corrected the correlation energy by 32(1)%.

Plots of the Morphed PES



HCN-HF isomer

$$R_e = 3.323(2) \text{ \AA}$$

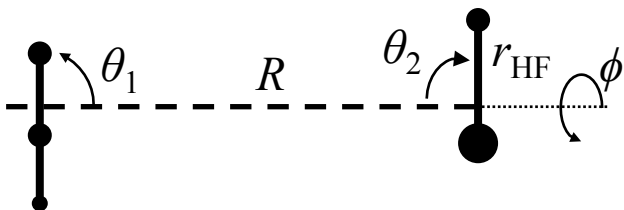
$$D_e = 2724(2) \text{ cm}^{-1}$$

HF-HCN bent isomer

$$R_e = 3.830(2) \text{ \AA}$$

$$D_e = 1108(4) \text{ cm}^{-1}$$

$$\text{Barrier high} = 488(10) \text{ cm}^{-1}$$



Predictions of vibrational frequencies

Observable (cm ⁻¹)	$V_{CMM-RC}^{(5)}$	Exp.	%Error
$3\nu_7^3$	219.27	220.1964(8)	0.42
$\nu_4 + \nu_7^1$	242.42	242.817(23)	0.16
$4\nu_7^4$	291.94	293.2278(9)	0.44
$2\nu_6^0$	1000.43	998.5287(3)	0.19
$2\nu_6^0 + \nu_4$	1138.65	1132.4738(12)	0.55
$2\nu_6^0 + 2\nu_4$	1251.22	1257.7374(8)	0.52
$\nu_1 + \nu_7^1 - \nu_7^1$	3720.19	3720.4278(33)	0.01
$\nu_1 + \nu_4 - \nu_4$	3728.17	3724.2368(53)	0.11
$\nu_1 + \nu_6^1$	4317.32	4320.3(1)	0.07
$\nu_1 + 2\nu_6^0$	4811.28	4814.9(1)	0.08

Conclusions

- A 5-D CMM-RC potential for HCN-HF.
- Band origin fundamental vibrational frequencies are fitted to near spectroscopic accuracy.
- The morphed potential demonstrate to be of high accuracy in predicting experimental frequencies.
- The CMM-RC method has the advantage of generating an accurate potential for B...HX complexes with less computational effort and expense than *ab initio* methods alone.

Acknowledgments

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