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

Pumping and probing vibrational modulated coupled electronic coherence in HCN using short UV fs laser pulses:

a 2D quantum nuclear dynamical study

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Supplementary materials

Table S1: Comparison of the relative energies of HNC and of the TS for the isomerization HCN-HNC with selected theoretical and experimental works.

Reference	Level of theory/experimental	E_{HNC}	E_{TS}
Rendell *et al.*[1]	CCSD(T)	0.64 eV	2.08 eV
Bowman *et al.*[2]	CCSD	0.65 eV	2.11 eV
Bowman *et al.*[3]	MR-SDCI-CASSCF	0.66 eV	1.98 eV
Knowles *et al.*[4]	MRCI	0.60 eV	1.76 eV
Nguyen *et al.*[5]	HEAT-456QP	0.65 eV	–
Hehre *et al.*[6]	Expt.	0.63± 0.09 eV	–
Hansel *et al.*[7]	Expt.	0.65 ± 0.04 eV	–
This work	SA-CASSCF(10,12) cc-pVTZ, 8 states	0.61 eV	2.21 eV

Computed energies are expressed relative to the energy of HCN at the GS equilibrium geometry.

Natural molecular orbitals of the active space

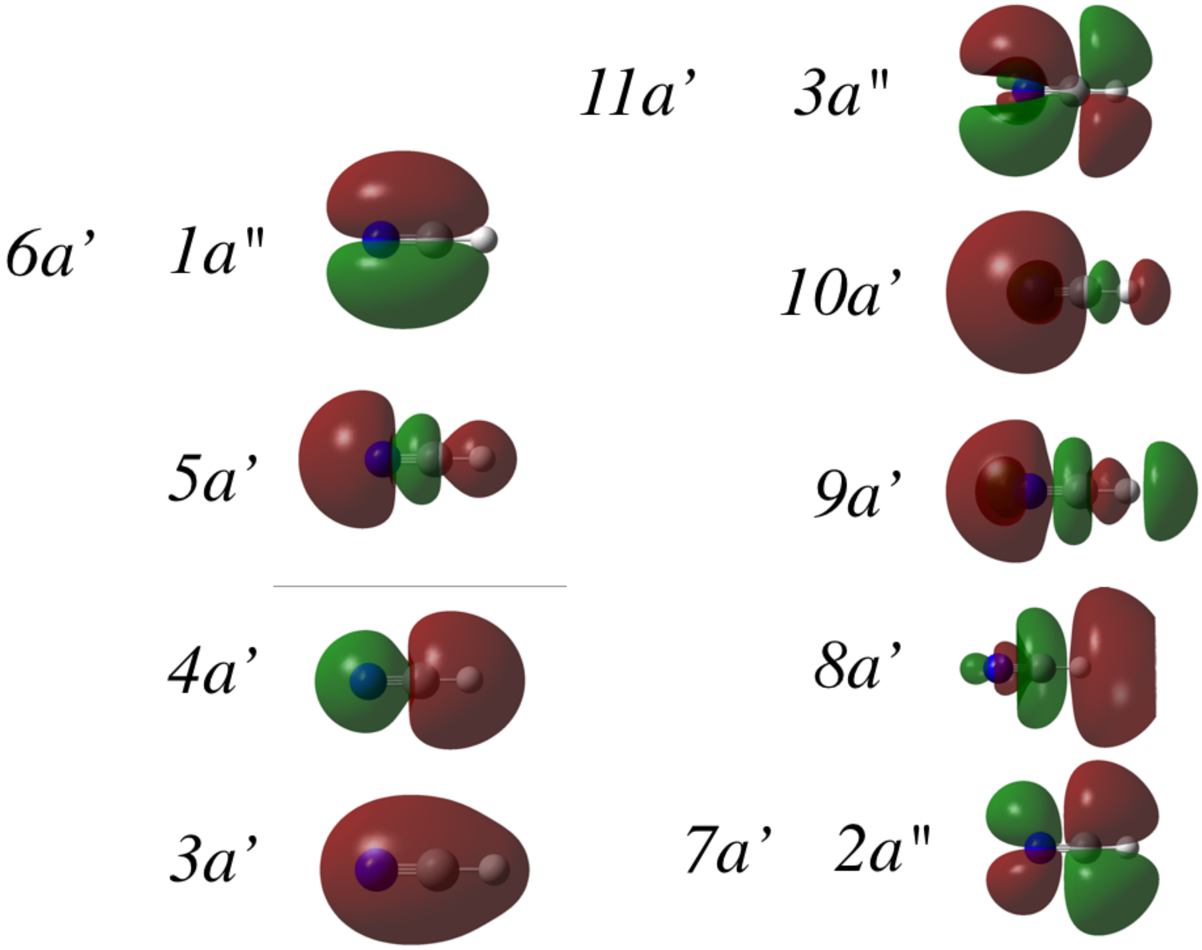


Figure S1 : Natural molecular orbitals included in the active space for the computation at the CASSCF(10,12) level using a cc-pVTZ basis-set. The lower 1*a*' and 2*a*' MO's are closed with an occupation number restricted to 2. The symmetry of the MO's is given in the C_s group.

Main configurations of the 6 lowest excited states

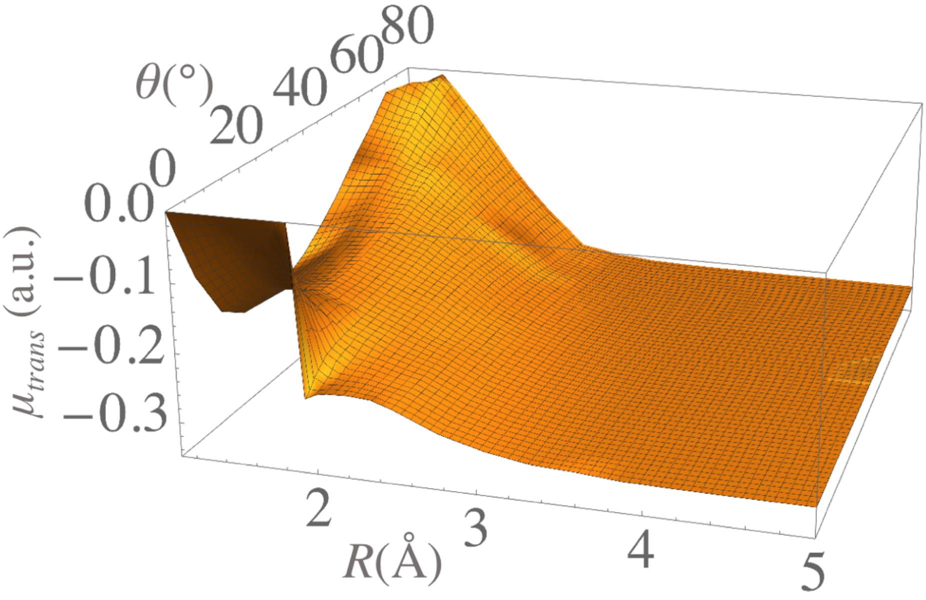
Table S2: Main configurations in the 6 lowest electronic states of HCN.

State		Main configurations	Vertical excitation energy (eV)	Correlation with CN
Cs	$C_{\infty v}$			
$1^1A'$	$^1\Sigma^+$	$(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^2$	0.00	$\tilde{X}\,^2\Sigma^+$
$1^1A''$	$^1\Sigma^-$	$(3a')^2(4a')^2(5a')^2(6a')^1(1a'')^2(2a'')^1$ $(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^1(7a')^1$	8.69	$\tilde{A}\,^2\Pi$
$2^1A'$	$^1\Delta$	$(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^1(2a'')^1$ $(3a')^2(4a')^2(5a')^2(6a')^1(1a'')^2(7a')^1$	8.97	$\tilde{A}\,^2\Pi$
$2^1A''$	$^1\Delta$	$(3a')^2(4a')^2(5a')^2(6a')^1(1a'')^2(2a'')^1$ $(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^1(7a')^1$	8.97	
$3^1A'$	$^1\Pi$	$(3a')^2(4a')^2(5a')^1(6a')^2(1a'')^2(7a')^1$	9.68	
$3^1A''$	$^1\Pi$	$(3a')^2(4a')^2(5a')^1(6a')^2(1a'')^2(2a'')^1$	9.68	

The correlation with the electronic states of CN is shown for the 3 lowest electronic states. The vertical excitation energy for each state is computed at the equilibrium energy of the GS.

Transition dipoles

The sign of the transition dipoles along the PES depends on the phase between the adiabatic eigenvectors of the electronic states. During the CASSCF optimization, this phase is not controlled, leading to changes in the sign of the transition dipoles along the PES. We corrected the sign of the dipole along the PES by computing the overlap between the eigenvectors along the PES and switching the sign of the transition dipoles when the phase of the electronic states changed along the PES. A similar procedure for correcting the sign of the transition dipoles was used in ref. [8] .



Figure

Figure S2 : Surface of the y component of the transition dipole moment between 1A’ and 1A”. In order to ensure a smooth variation of the transition dipole moments as a function of R and θ , we checked for changes of sign in the phase of the adiabatic eigenvectors of the electronic states by computing their overlap.

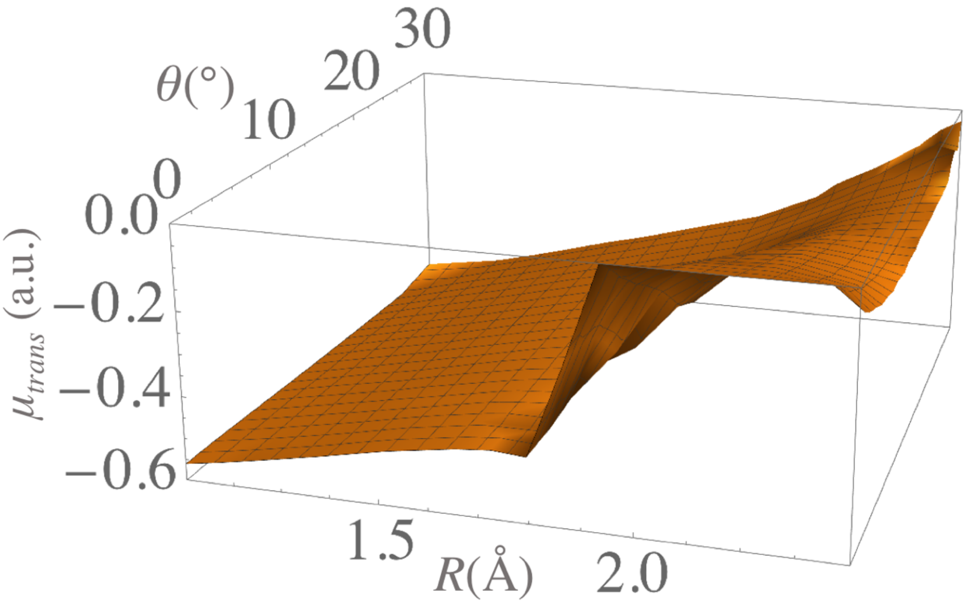


Figure S3 : Surface of the y component of transition dipole moment between 1A’ and 3A”. In order to ensure a smooth variation of the transition dipole moments as a function of R and θ , we checked for changes of sign in the phase of the adiabatic eigenvectors of the electronic states by computing their overlap.

Potential energy surfaces in polar coordinates

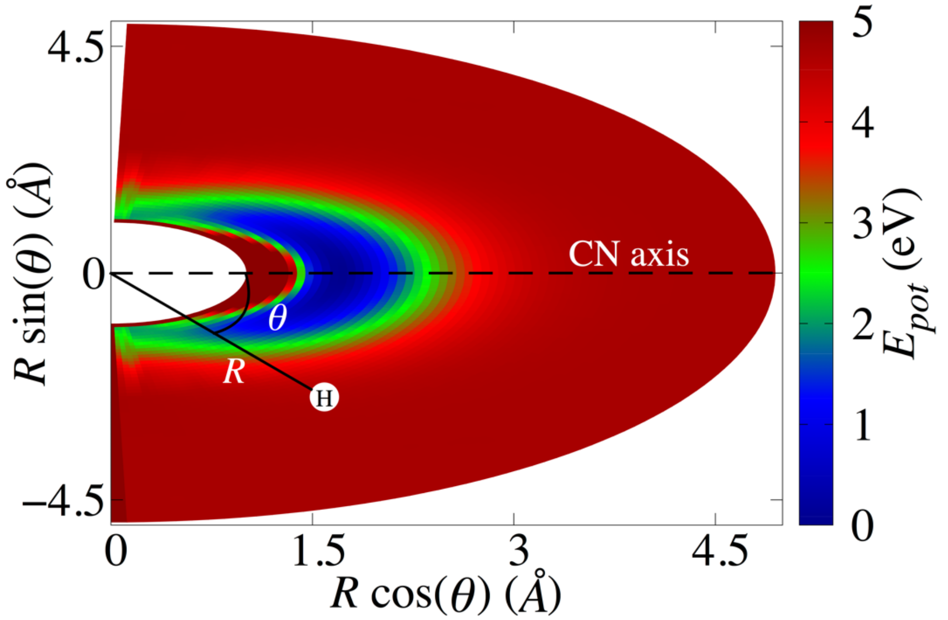


Figure S4 : Potential energy surface of the ground electronic state GS(1A') in the region of the HCN well in polar coordinates. The *x* axis is the projection of the position of the H atom on the CN axis and the *y* axis is the projection on the axis perpendicular to CN.

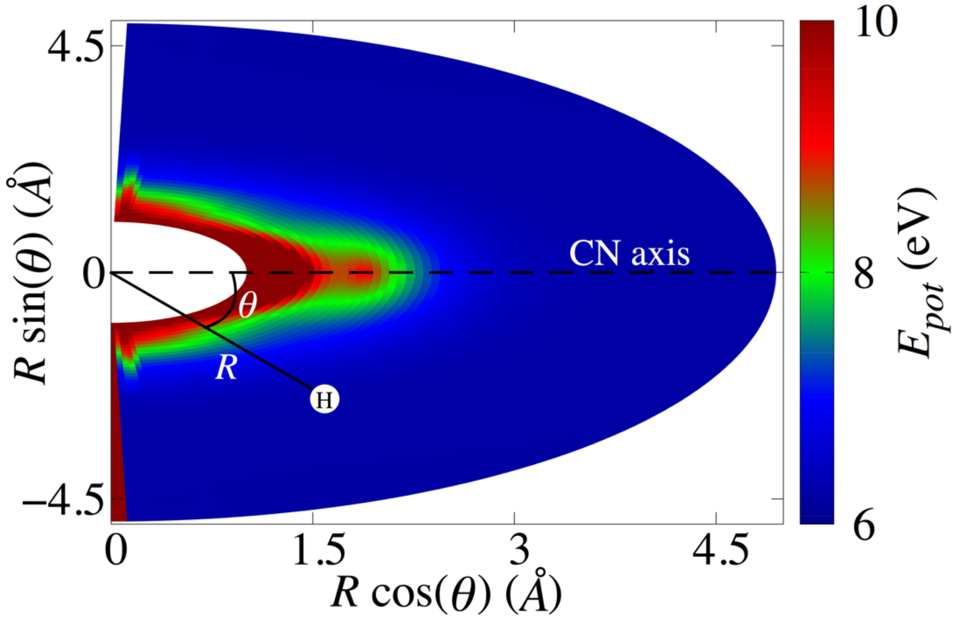


Figure S5: Potential energy surface of the first excited electronic state 1ES (1A") in the region of the HCN well in polar coordinates. The *x* axis is the projection on the CN axis and the *y* axis is the projection on the axis perpendicular to CN, of the position of the H atom.

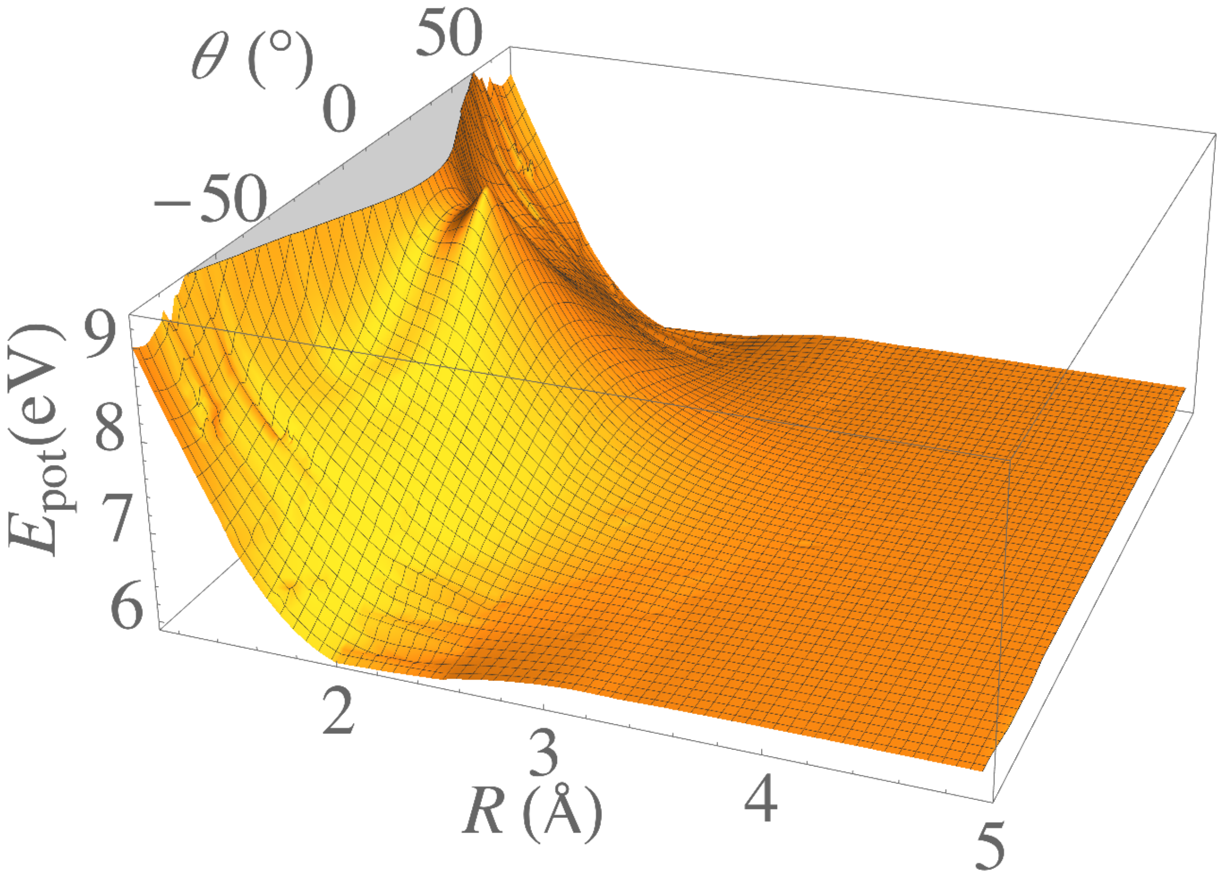


Figure S6: PES of the 2ES(2A') in the region of the HCN well.

References

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