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Vibrationally quantum-state-specific reaction dynamics of H atom abstraction by CN radical in solution

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Supporting Online Material

Methods

Experiments were conducted using the ULTRA laser system at the Central Laser Facility at the Rutherford Appleton Laboratory. The capabilities and specifications of the ULTRA cluster are described in detail elsewhere (S1, S2), but in brief, a 65 MHz titanium:sapphire oscillator synchronously seeded a pair of regenerative amplifiers (Thales) operating at 10 kHz repetition rate. One amplifier was configured to produce 40–80 fs duration pulses with broad bandwidth, and the second produced longer pulses of ~1 ps duration and narrower bandwidth. Third harmonic generation of part of the 800 nm output from the femtosecond amplifier produced UV pulses at 266-nm. Approximately 0.4 mJ of the 50-fs, broadband output pulse train pumped a TOPAS OPA, and difference frequency mixing of the signal and idler components generated mid-IR pulses with ~500 cm⁻¹ bandwidth and ~50 fs pulse duration at the output of the OPA. In experiments involving an IR-pump and IR-probe configuration, the
~2 ps duration, narrow bandwidth (10 – 12 cm\(^{-1}\)) IR pump light was generated by pumping a second TOPAS OPA with the pulse train from the amplifier producing the ps pulses.

Reaction was initiated in solutions of ICN and cyclohexane in chlorinated solvents (CHCl\(_3\), CH\(_2\)Cl\(_2\) or CDCl\(_3\)) using a ~50 fs UV laser pulse (typically at a wavelength of 266 nm) linearly polarized at magic angle to the IR probe laser polarization. The UV pump beam energies were \(\leq 2\ \mu J\) per pulse, and the UV and IR beam diameters at the sample were, respectively, ~70 and 100 \(\mu m\). The 266-nm photodissociation of gas-phase ICN produces CN radicals of which ~98% are in their ground vibrational level (\(S3\)). The insolubility of ICN in cyclohexane prevented study of the reaction dynamics in the absence of a chlorinated solvent. Transient IR spectra were obtained in absorption using an IR pulse with a bandwidth of ~500 cm\(^{-1}\) and a center wavenumber selected to probe the C-H stretching region (~3260 cm\(^{-1}\)) of HCN, the C-N stretching region (~2095 cm\(^{-1}\) in HCN, 1920 cm\(^{-1}\) in DCN) or the C-D stretching region (~2600 cm\(^{-1}\)) of DCN. The IR radiation transmitted by the solution was dispersed by a grating onto a pair of 128-element mercury-cadmium telluride array detectors (IR Associates), providing full (i.e. ~500 cm\(^{-1}\)) spectral coverage with every laser pulse. The overall instrument response time was ~200 fs. A reference spectrum of the laser pulse was accumulated on a third, 64-element array detector and used to remove the effects of laser fluctuations from transient absorption data. Shot-to-shot subtraction methods removed solvent absorption bands and identified transient features resulting from the UV-initiated chemistry. Measurements were made in a Harrick cell with 0.38-mm thick spacer and BaF\(_2\) windows, through which the sample was continuously circulated by a peristaltic pump. In all experiments, the initial ICN concentration was 0.14 M, and the concentration of the cyclohexane was 0.5, 1.0 or 1.5 M. Spectra were obtained at selected, but randomly ordered, time delays between the UV and IR pulses in the range 1 – 1000 ps. Anharmonicity of the
modes of HCN ensured that absorption bands corresponding to vibrational ground state and vibrationally excited molecules could be distinguished clearly in the spectra. The IR absorption bands of the solvent did not overlap significantly the HCN bands studied. The low extinction coefficient of ICN necessitated use of high intensity UV pulses to generate CN radicals. This resulted in the HCN transient signal being offset by a substantial background signal, and the data presented here have had this offset subtracted. The subtraction leaves residual patterns that can be observed in most of the spectra presented, but that do not obscure the analysis.

A linear pixel to wavelength calibration of each spectrum was performed by obtaining IR absorption spectra of static samples such as pure 1,4-dioxane or cis-stilbene using the broadband IR laser pulses and the spectrometers and array detectors described above. For each static sample, an FTIR spectrum was also recorded in a commercial spectrometer with 1 cm\(^{-1}\) spectral resolution to provide absolute calibration. The spectra were then placed on a wavenumber scale by direct conversion from wavelength.

In what follows, the notation HCN(\(v_1v_2v_3\)) specifies the number of quanta of the three vibrational modes of HCN, the C-N stretch (\(v_1\)), the bend (\(v_2\)) and the C-H stretch (\(v_3\)), and equivalently for DCN. The vibrational relaxation rates of HCN(100) and HCN(001) were separately measured in all three solvents using an IR pump and probe experiment in which HCN in solution was excited to \(v_1=1\) or \(v_3=1\) by a narrow bandwidth laser pulse, and probed in absorption by the broadband IR pulse delayed by up to 1000 ps. Equivalent measurements were also made for DCN in CHCl\(_3\). In all experiments, the solutions used were the same as for the reactive studies (i.e. a solution of ICN and cyclohexane or \(d_{12}\)-cyclohexane in CH\(_2\)Cl\(_2\), CHCl\(_3\) or CDCl\(_3\)). The HCN was prepared by irradiating the sample with 2-cm diameter, 40
mW power, 266-nm wavelength light from a 10 kHz, nanosecond pulse duration microlaser for ~15 mins immediately prior to the IR pump and probe studies. The transient IR spectra showed bi-exponential decays of band intensity, with a short-time relaxation (with time constant <5 ps) that may be a consequence of relaxation of molecular axis polarization by rotational diffusion, and a slower decay that is attributed to the vibrational relaxation. The time constants reported in the main paper are for the slower component of the bi-exponential decay; as these lie in the range 100 – 300 ps, they are well separated from the rapid, early time decay component. All uncertainties quoted in the time constants are 1 standard deviation (1 SD) of values derived from fits to 3 to 6 separate data sets.

There is no clear-cut evidence from the IR pump and probe spectra of coupling of the C-H stretching vibrational energy into the lower-frequency HCN bending mode, the signature of which would be development of a shoulder on the low-frequency side of the $3^1 \tilde{g}$ band corresponding to the $2^1 \tilde{g} + 3^1 \tilde{u}$ combination with a diagonal hot band in the bending motion. We were, however, able to observe coupling of the C-H excitation into the C-N stretching mode with a time constant of ~200 ps by IR excitation of the C-H stretch and IR probing in the C-N stretching region.

**Assignment of spectra**

Calibrated IR absorption spectra were assigned using a standard expression for the vibrational energy levels of HCN or DCN (S4) to compute transition wavenumbers between vibrational levels. The evaluation of this expression used spectroscopic constants (harmonic wavenumbers, diagonal and off-diagonal anharmonic corrections and vibrational angular momentum terms) from references (S5, S6). Solvent shifts (~48 cm$^{-1}$ for the C-H stretch and ~3 cm$^{-1}$ for the CN stretch in CH$_2$Cl$_2$, with similar values in other solvents) were calculated
using the difference between the gas-phase spectroscopic frequencies of vibrational fundamental bands and the observed positions of these bands in HCN samples in the various solvents employed. These shifts were assumed to be the same for other transitions in the same spectral region such as pure hot bands of the same vibrational mode or combinations of the fundamental transitions with diagonal hot bands of other vibrational modes.

In the C-H stretching region of HCN there is some potential ambiguity in the assignment of combination bands that appear as shoulders on the low wavenumber side of the $3^1_0$ fundamental and $3^2_1$ hot bands. The frequencies and time-dependencies of the shoulders are consistent with combination bands that are either diagonal in the bending vibration (i.e. of the type $2n^3_0$ and $2n^3_1$) or the C-N stretching mode (i.e. $1n^3_0$ and $1n^3_1$), with the small shifts to lower wavenumber than the pure C-H stretching bands caused by anharmonic coupling of the modes. These anharmonic couplings are such that these bands cannot be resolved spectroscopically. We make the former assignment, guided by the observation from gas-phase studies of reaction of CN radicals with hydrocarbons which show extensive excitation of the HCN bending mode ($S7$-$S10$). For example, for the reaction $\text{CN} + \text{C}_2\text{H}_6 \rightarrow \text{HCN} + \text{C}_2\text{H}_5$, Bethardy et al. ($S9$) reported that $>99\%$ of the HCN products have at least one quantum of bending vibrational excitation, and for the $\text{CN} + \text{CH}_4 \rightarrow \text{HCN} + \text{CH}_3$ reaction the fraction was measured to be $\sim 80\%$ ($S10$). In the C-H stretching spectral region, there is no absorption at the wavenumbers expected for bands originating from HCN($1n0$) and HCN($2n0$), indicating that the HCN is not formed solely with C-N stretching and bending excitation. Our assignment is further supported by the absence of any clear evidence for C-N stretching excitation in spectra obtained in the wavenumber region of the $v_1$ vibrational mode (see figure 4 of the main paper and associated discussion).
Spectral assignments in figure 2 of the main paper indicate that the highest bending level for which signal was observed above the baseline corresponds to a vibrational quantum number $v_2=2$. Searches of the spectral region to lower wavenumber than displayed in this figure revealed no evidence for signals from absorption by HCN molecules with C-H stretching excitation corresponding to $v_3=2$ or higher. This search is complicated in CH$_2$Cl$_2$ by overlapping but weak solvent bands, but the region is free from solvent interference in CDCl$_3$. Signal-to-noise ratios in the spectra place an upper limit of ~10% on the formation of HCN in vibrational levels with $v_2\geq 3$ or $v_3\geq 2$. The prompt rise of signals in the $3^1_1$ and $2^m_2^2_1$ bands (see below and the main paper) is also strongly indicative of preferential formation of HCN($v_3=1$) directly by the chemical reaction, not by vibrational relaxation of more highly vibrationally excited molecules which we expect to occur on timescales of >100 ps. This inference is reinforced by the kinetic analysis described in the following section.

In the C-N stretching region, a bleach signal is observed at 2176 cm$^{-1}$ that is attributed to ICN. A band at 2065 cm$^{-1}$ that grows in with time is assigned to INC, which can form by recombination of CN radicals and I atoms from ICN photolysis (S11). This band is present in the absence of cyclohexane. The spectra show no evidence for ClCN formation from reaction with the solvent (ClCN is expected to exhibit a fundamental band at ~2208 cm$^{-1}$). A weak transient feature observed at 1877 cm$^{-1}$ for DCN (from CN reaction with $d_{12}$-cyclohexane in CHCl$_3$) shows a fast initial rise followed by a decay in intensity with time constant of 172 ± 30 ps (1 SD uncertainty). Assignment to the $1^2_1$ hot band in the C-N stretch is discounted because, with allowance for a solvent shift, this band should lie at 1905 cm$^{-1}$. The most plausible assignment, based on known vibrational frequencies, is to the $1^2_1^2_1^2_1^1$ or $1^2_1^2_2^m_2^2_1^1$ transitions, which is consistent with early time excitation of the C-D stretching and the bending modes of the DCN.
The growth of intensity in the $1^3_0$ band of HCN, such as is shown for feature A in figure 4 of the main paper, was examined for the case of CN + c-C$_6$H$_{12}$ reaction in CDCl$_3$ solvent. In this choice of solvent, the relaxation times for C-N and C-H stretching excitation differ by a factor of ~two (122 ± 20 and 265 ± 20 ps respectively; 1 SD uncertainties) as determined from the IR pump and probe experiments. The temporal rise in $1^3_0$ intensity from 200 ps onwards is much better modelled using a time constant $\tau = 265$ ps than $\tau = 122$ ps, indicating that the HCN(000) probed in this band is formed by relaxation of C-H (and not C-N) stretch excited nascent products. This outcome is consistent with the picture of the reaction dynamics causing excitation of the C-H stretching mode of HCN, with the C-N mode remaining unexcited, and therefore a spectator mode.

**Kinetic model and fitting of kinetic data**

The reaction scheme in Table S1 was adopted in analysis of the time-dependence of spectral features in the HCN products of the reactions of CN radicals with cyclohexane.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN + c-C$<em>6$H$</em>{12}$ $\rightarrow$ HCN(0n1) + c-C$<em>6$H$</em>{11}$</td>
<td>1 $k_1$</td>
</tr>
<tr>
<td>CN + c-C$<em>6$H$</em>{12}$ $\rightarrow$ HCN(001) + c-C$<em>6$H$</em>{11}$</td>
<td>2 $k_2$</td>
</tr>
<tr>
<td>CN + c-C$<em>6$H$</em>{12}$ $\rightarrow$ HCN(0n0) + c-C$<em>6$H$</em>{11}$</td>
<td>3 $k_3$</td>
</tr>
<tr>
<td>CN + c-C$<em>6$H$</em>{12}$ $\rightarrow$ HCN(000) + c-C$<em>6$H$</em>{11}$</td>
<td>4 $k_4$</td>
</tr>
<tr>
<td>HCN(0n1) $\rightarrow$ HCN(001)</td>
<td>5 $k_5$</td>
</tr>
<tr>
<td>HCN(0n1) $\rightarrow$ HCN(0n0)</td>
<td>6 $k_6$</td>
</tr>
<tr>
<td>HCN(001) $\rightarrow$ HCN(000)</td>
<td>7 $k_7$</td>
</tr>
<tr>
<td>HCN(0n0) $\rightarrow$ HCN(000)</td>
<td>8 $k_8$</td>
</tr>
</tbody>
</table>

Table S1: Kinetic scheme for the reaction of CN with cyclohexane and subsequent vibration relaxation of HCN products
The number of quanta of bending vibration is specified either as \( n \) (which takes values 1 – 2) or 0 because the bending hot bands are only partially resolved in the experimental spectra. Processes 1 – 4 are bimolecular chemical reactions that produce HCN in specific sets of vibrational levels, and processes 5 – 8 are state-resolved vibrational relaxation steps involving loss of energy to the surrounding solvent (not explicitly represented in the scheme). Excitation of, and coupling to, the C-N stretch were excluded from the model, as were other intramolecular couplings between vibrational modes that might allow, for example, relaxation of the C-H stretch into bending vibrations (see earlier). The model is therefore likely to be a simplification of the full mechanism for reaction and relaxation, but captures the most significant components.

Reactions 1 – 4 are treated as pseudo first-order processes because the cyclohexane is in considerable excess over the CN radicals. The vibrational relaxation steps 5 – 8 are also treated as first order because of the excess of solvent molecules. A set of differential equations for the above kinetic scheme can be solved analytically for the time-dependence of the concentrations of HCN in the different vibrational levels. These analytical expressions formed the basis of fits to data sets such as those shown in figure 3 of the main paper to derive rate coefficients \( k_1 \) – \( k_8 \). To constrain the fits, the rate coefficients for loss of a quantum of C-H stretching excitation (\( k_6 \) and \( k_7 \)) were fixed at the values measured by IR pump and IR probe spectroscopy for HCN in the appropriate solvent (figure 1 of the main paper). The fitting of the time-dependent IR intensity data must also take into account two further factors: (i) the IR absorption intensities depend on the difference in population between the connected vibrational levels; (ii) the IR transition dipole moments (TDMs) for vibrational ground state and vibrationally excited HCN differ. To address the first point, the
integrated rate expressions were adapted to give expressions for population differences prior to fitting to data sets. Fixed ratios of calculated TDMs (S12) for the $3^2_1$ hot band of the C-H (or C-D) stretch and the $3^1_0$ C-H (C-D) stretching fundamental were incorporated into the initial fits of the amplitudes of the data sets, with the bending vibrational hot bands assumed not to perturb the C-H TDMs in combination bands. The ratio of TDMs for the $3^2_1$ and $3^1_0$ bands was calculated by Botschwina (S12) to be 1.76, but the IR-pump and IR-probe spectra shown in figure 1 of the main paper suggest a value closer to unity that may indicate need for revision of this calculated value, or may reflect some contribution of stimulated emission to the $3^1_0$ band intensity. We therefore allowed the TDM ratio value to float in fits to reaction data (e.g. fig 3 of the main paper), and, for fits to several data sets, obtained TDM ratios in the range 1.0 – 1.2. The quality of fits, especially to early-time band intensities, was improved by floating this parameter as well as the rate coefficients discussed above.

All the rate coefficients have specified uncertainties that are 1 SD from fits to 4 (for CH$_2$Cl$_2$ solvent) or 6 (for CDCl$_3$ solvent) separate data sets. The fits are weighted by the error bars on individual data points (as displayed in figure 2 of the main paper) which are derived from the integration of IR band intensities by least-squares fitting to Gaussian functions as described in the main paper, and are taken as twice the least-squares fitting uncertainty.

The experimental spectra indicate that the highest populated level of the bending mode of HCN is $v_2$=2 (with perhaps some $v_2$=3 for reaction in CDCl$_3$). To keep the kinetic model tractable, single quantum relaxations of bending vibrational levels lying at or above $v_2$ =1 (i.e. $v_2 = n$ to $v_2 = n - 1$ for $n \geq 1$) were not treated separately in the scheme. Instead the time dependence of the integrated intensity for overlapping spectral features arising from all these bend-excited levels was analysed. The rate coefficients $k_5$ and $k_8$ describe recovery of HCN
with \( v_2 = 0 \), which, in our single-quantum relaxation model, occurs by \( v_2 = 1 \rightarrow v_2 = 0 \) but the population of \( v_2 = 1 \) is potentially replenished by the cascading process \( v_2 = n \rightarrow v_2 = n-1 \rightarrow \ldots \rightarrow v_2 = 1 \). The model also neglects any intramolecular vibrational redistribution (IVR) from the stretching modes to the lower frequency bending mode; the IR-pump and IR-probe experiments in the C-H stretching region show no evidence of significant IVR of this type (e.g. as a shoulder developing on the \( 3_1^2 \) band). The time constants obtained from rate coefficients derived from fits to the intensities of the bending vibrational features (specifically \( k_3 \) and \( k_8 \) in the model) may therefore be longer than the true time constants for single-step relaxations of the bending vibration.

To test for possible formation of more highly vibrationally excited reaction products than the kinetic model considers, numerical integration was carried out of an extended model in which the possible formation of HCN(0\( n_2 \)) by reaction and the subsequent relaxation to HCN(0\( n_1 \)) were included. The resultant fits indicate \(<10\%\) excitation of \( v_3=2 \) from the chemical reaction (consistent with deductions from the signal-to-noise ratios in the transient IR spectra), and require single-quantum relaxation rates of this vibrational mode to be an order of magnitude faster for \( v_3=2 \rightarrow v_3=1 \) than for \( v_3=1 \rightarrow v_3=0 \). The production of HCN(0\( n_2 \)) from the reaction was therefore discounted as a significant channel.

The reactions of CN with c-C\(_6\)H\(_{12}\) in solution in CH\(_2\)Cl\(_2\) (but not in CDCl\(_3\)) will produce HCN not only from H-atom abstraction from cyclohexane but also from the solvent. In all experiments, the addition of cyclohexane enhances the yield of HCN by a factor of at least two over the yield from reaction with the solvent, despite the \( \leq 1.5 \text{ M} \) concentration of cyclohexane. Pure liquid CH\(_2\)Cl\(_2\) is 15.6 M. To isolate the reactions of CN with c-C\(_6\)H\(_{12}\) the following procedure was adopted. Experiments were carried out on a solution of 0.14 M ICN
with 0.75 – 1.5 M cyclohexane in the chlorinated solvent, and were then immediately followed by identical measurements for 0.14 M solutions of ICN in the chlorinated solvent without cyclohexane. Transient IR spectra were fitted as described above and in the main paper for all time delays. The HCN absorbances for individual features in the IR spectra for the ICN solution were then subtracted from those for the ICN / c-C₆H₁₂ solution in the same solvent (with minor correction for the slightly lower molarity of the solvent in the solution containing cyclohexane) at each time delay. The resultant time-dependent data sets were fitted to the kinetic model described above. This procedure is validated by comparison with the results obtained for reactions in CDCl₃, for which the solvent-reaction channel is not observed in the C-H stretching spectral region. Representative time-dependent spectra for reaction of CN radicals with c-C₆H₁₂ in CDCl₃ are shown in figure S1, with fits in figure S2.

Figure S1: Transient IR spectra of HCN from the reaction of CN + c-C₆H₁₂ in CDCl₃. The spectra were obtained in the C-H stretching region. The solution consisted of 0.14 M ICN and 1.5 M c-C₆H₁₂. The combs above the spectra indicate spectroscopic assignments. The sharp dips in the spectra at ~3150 cm⁻¹ are caused by a weak solvent band. Weak oscillatory structure in the spectra obtained at longer time delays results from interference effects in the IR optical path.
Figure S2: The upper panel shows fits (solid lines) to the kinetic model outlined in the main text of the time-dependent IR band intensities (symbols) for the spectra in figure S1. These spectra were obtained for the CN + c-C₆H₁₂ reaction in CDCl₃. Blue is HCN(0n1) (n=1,2); red is HCN(001); purple is HCN(0n0) and black is HCN(000). The kinetic model is summarized in the lower panel together with derived values of the rate coefficients. Uncertainties in the rate coefficients are ±1 SD of values derived from fits to six data sets. The error bars on individual data points in the upper panel are twice the least squares fitting error to Gaussian spectral lineshape functions. In the fits, k₆ and k₇ were constrained to the values obtained from IR pump and IR probe experiments described in the main paper.

**Computational investigations of reaction energetics and dynamics**

To investigate energy disposal in the products of CN radical reactions with alkanes under gas-phase conditions, and therefore to provide benchmark dynamics against which the behavior in solution can be compared, we carried out theoretical modelling of the CN + C₃H₈ → HCN + C₃H₇ reaction. All wavefunction calculations were carried out using the MOLPRO suite of programs (S13), and all DFT calculations were carried out using the G03 suite of programs (S14). Reference zero point energies and relaxed scans along the secondary H-CN coordinate were obtained using the UCCSD-ROHF/cc-pVDZ method, giving a reaction
enthalpy of $-28.4$ kcal mol$^{-1}$, in agreement with the experimental value of $-29$ kcal mol$^{-1}$ ($S15-S17$). The minimum energy association path has a linear H-CN geometry. As is shown in figure S3, the reaction has no abstraction barrier for the central H atoms on propane.

![Figure S3: Relaxed-scan energies along the C-H distance at the CCSD(T) / complete basis limit, and the re-parameterized BB1K functional used in the direct dynamics calculations described in the text.](image)

A BB1K functional modified to have 56% exact Hartree-Fock exchange along with the 6-31G$^*$ basis set gave energies in reasonable agreement with the UCCSD-ROHF results (see Figure S3). Using this functional, we carried out quasi-classical trajectory calculations with a locally modified version of the VENUS dynamics package ($S18$, $S19$). Coordinates and momenta for CN and propane reagents were selected using microcanonical normal mode sampling ($S20$). Initial normal mode quantum numbers, rotational energies, and translational energies were selected from 298 K Boltzmann distributions. Trajectories began with a 4.5 Å center-of-mass separation between CN and propane fragments, each of which had a randomly sampled rotational orientation. To reduce the computational expense of the direct dynamics, and given that our primary interest in this work was the post transition state (TS) dynamics, we: (i) set the impact factor to zero, and (ii) used importance sampling to increase the probability of selecting reactive trajectories. Trajectories which satisfied the importance sampling criteria were propagated 3000 steps using a velocity Verlet integrator and a
timestep of 0.2 fs. Trajectories which did not have a total energy conservation of better than 2.5% with respect to the final HCN + C_3H_7 potential energy were discarded, leaving a total of 56 reactive trajectories.

Energy disposal in the nascent HCN was determined by projecting its kinetic energy and geometry into the 3N-5 Cartesian normal mode displacements of equilibrium HCN. The averaged results presented in Table S2 show that the HCN rotational and translational energies are very close to their thermal values at 298 K. Much of the excess energy goes into HCN vibrational excitation, with \( v_3 \sim 1 \) in the H-C stretch, and significant excitation (\( v_2 \sim 4 \)) in the HCN bending mode. The bend excitation derives from a soft bending potential in the region of the variational association TS. Figure S4 displays a histogram of the distribution of angles in the region of the association TS for those trajectories going to HCN products. The angular distribution deviates significantly from the linear value of 180° obtained from relaxed scans along the minimum energy path.

Figure S4: Histogram of the distribution of H-C-N bend angles at a 1.8 Å H–C separation corresponding to the region of the variational association TS.
### Table S2: Average energy disposal in HCN vibrational, rotational, and translational degrees of freedom.

The approximate quantum numbers in the final column were obtained by subtracting the harmonic zero point energy from the average total energy, and then dividing by the energy of the harmonic vibrational frequency. The frequencies in the third column are those derived from the calculations.

<table>
<thead>
<tr>
<th>Degree of freedom (degeneracy)</th>
<th>Designation of mode</th>
<th>Frequency /cm(^{-1})</th>
<th>Average total energy /kcal mol(^{-1})</th>
<th>Approximate (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1) (1)</td>
<td>C-N stretch</td>
<td>2349.1</td>
<td>6.8</td>
<td>0.51</td>
</tr>
<tr>
<td>(v_2) (2)</td>
<td>Bend</td>
<td>826.0</td>
<td>10.5</td>
<td>3.95</td>
</tr>
<tr>
<td>(v_3) (1)</td>
<td>C-H stretch</td>
<td>3612.0</td>
<td>12.9</td>
<td>0.75</td>
</tr>
<tr>
<td>Rotations (2)</td>
<td></td>
<td></td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>Translations (3)</td>
<td></td>
<td></td>
<td></td>
<td>2.6</td>
</tr>
</tbody>
</table>

In order to obtain insight into relative solvent effects on the CN + cyclohexane potential energy surface with respect to the gas phase, we ran classical molecular dynamics simulations using a locally modified version of the CHARMM software suite (S21). The reactive CN + cyclohexane potential was obtained using the empirical valence bond (EVB) method (S22, S23). The diagonal elements of the Hamiltonian matrix were obtained using the Merck Molecular Mechanics force-field (MMFF) implementation in CHARMM (S24). Relative energy offsets and coupling elements of the EVB Hamiltonian were determined through non-linear least squares fitting of relaxed PES scans against the data shown in Figure S3. The coupling elements were chosen to be a linear combination of two one-dimensional Gaussian functions (S25).

In the solution-phase simulations, CN and cyclohexane were solvated within a 23.7 Å\(^3\) periodic box filled with 125 molecules of CH\(_2\)Cl\(_2\), which corresponds to the experimental
298K CH$_2$Cl$_2$ density of 1.33 g ml$^{-3}$ (S26). To obtain the potential of mean force (PMF) along the C-H stretch in both the gas-phase and the solution-phase simulations, we used the recently developed BXD algorithm (S27), which we have implemented in CHARMM. Equilibrium classical dynamics within each box were propagated using a Langevin equation with a 298 K thermostat, and convergence was monitored on each pass through the boxed phase space. Figure S5 shows the relative PMF in both the gas-phase and solution-phase simulations. Despite the fact that the association is an energetically barrierless process, both the gas-phase and solution-phase simulations show a maximum in the PMF at 1.8 Å, which we have shown as the zero for both surfaces. The origin of this maximum is primarily entropic (S28), corresponding to a reduction in relative fragment rotational and translation degrees of freedom as CN approaches cyclohexane to abstract a hydrogen atom. The figure shows that the energetics and barrier location on the solution-phase PMF are very similar to those of the corresponding gas-phase PMF. While the solution and gas-phase PMFs show some differences, linked to the screening of the interactions between reactants in the solution calculations, these differences are not particularly relevant for the HCN post transition state dynamics, as the maximum in the PMF lies at the same distance in both cases. In addition, inspection of the BXD calculations shows similar structures for the gas phase and solvated reactive species in the neighborhood of the transition state. Taken together, these observations suggest that the gross features of the dynamics en route to products should be substantially similar in solution and in the gas phase.
Figure S5: Potentials of mean force (PMF) along the coordinate for the new C–H bond formed in the reaction of CN radical with cyclohexane. PMFs are shown for the gas-phase reaction (solid line) and reaction in solution in CH$_2$Cl$_2$, and are plotted in units of RT where R is the gas constant and T = 298 K.

Animations of time-dependent IR spectra

The time-dependences of the various spectral features observed in the experiments are more evidently appreciated from animated plots of time-sequences of IR spectra than from static plots. Examples of such time sequences are therefore presented as separate QuickTime movie files to demonstrate the early time formation of vibrationally excited HCN and its subsequent relaxation to the vibrational ground state.

References


QuickTime movie files

1197796s1.mov – an animation of transient IR spectra of HCN in solution in CH$_2$Cl$_2$ showing the temporal behaviour in the C-H stretching region following IR excitation on the fundamental C-H stretching mode absorption. The data correspond to those plotted in Figure 1A of the main article.

1197796s2.mov – an animation of transient IR spectra of HCN in solution in CH$_2$Cl$_2$ showing the temporal behaviour in the C-N stretching region following IR excitation on the fundamental C-N stretching mode absorption. The data correspond to those plotted in Figure 1B of the main article.

1197796s3.mov – animations of transient IR spectra, obtained in the C-H stretching region, of HCN products of UV-laser initiated CN reactions in a 1.0 M solution of cyclohexane in CH$_2$Cl$_2$ (upper row) and pure CH$_2$Cl$_2$ (lower row). The combs above the spectra indicate spectroscopic assignments. The data correspond to those plotted in Figure 2 of the main article.

1197796s4.mov – an animation of the time-dependent IR spectra, obtained in the C-N stretching region, of HCN products of UV-laser initiated CN reaction with c-C$_6$H$_{12}$ in CH$_2$Cl$_2$. Feature A is the $1^1_0$ band in HCN. Bands B and C, centered at 2065 and 2037 cm$^{-1}$, are assigned, respectively, to INC and to CN radicals, which may be complexed with the solvent. The data correspond to those plotted in the upper panel of Figure 4 of the main article.
1197796s5.mov – an animation of the time-dependent IR spectra, obtained in the C-N stretching region, of DCN products of UV-laser initiated CN reaction with c-C₆D₁₂ in CHCl₃.

Feature D is the $1^1_0$ band in DCN. The bands in the region indicated as E are hot bands of $v_1$ and combinations of the $1^1_0$ transition with hot bands of the other two modes. Band F is discussed in the main text. The dips at 1899 and 1946 cm⁻¹ are solvent absorption induced transient signals. The data correspond to those plotted in the lower panel of Figure 4 of the main article.