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# Inelastic Scattering of CN Radicals at the Gas-Liquid Interface Probed by Frequency-Modulated Absorption Spectroscopy

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## **ABSTRACT**

We describe the results of the first application of frequency-modulated (FM) absorption spectroscopy to molecular scattering dynamics at a gas-liquid interface. A pulsed direct-current electric discharge of a supersonic expansion of BrCN seeded in He was used to generate a pulsed molecular beam of rotationally cold  $\text{CN}(X^2\Sigma^+)$  radicals, with a mean laboratory-frame kinetic energy of  $43.5 \text{ kJ mol}^{-1}$ . The molecular beam was directed at normal incidence onto a continually refreshed perfluoropolyether liquid surface. FM absorption spectroscopy on the  $\text{CN}(A^2\Pi-X^2\Sigma^+)$  (2,0) band was used to measure Doppler lineshapes for individual CN rotational states as a function of time after the DC discharge pulse. This enabled the characterization of both the incident molecular beam and inelastically surface-scattered CN rotational and translational energy

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3 distributions. The surface-scattered CN rotational distribution is well-characterized by a single  
4 temperature of  $850 \pm 130$  K. The translational distributions perpendicular to the surface normal  
5 are non-Maxwellian, and are substantially superthermal. We interpret these observations as the  
6 result of *impulsive scattering* being the dominant mechanism, similar to our previous independent  
7 measurements of OD inelastic scattering at liquid surfaces. Within the current limitations of signal-  
8 to-noise, no clear evidence for a discrete component from *thermal desorption* is observed, in  
9 contrast to previous literature measurements of NO and CO<sub>2</sub> scattering at perfluoropolyether  
10 surfaces.  
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## 26 INTRODUCTION

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29 Interactions between gas-phase molecules and liquid surfaces are common and practically  
30 important in a wide range of biological, technological and natural environments. Examples include  
31 respiration, distillation, gas separation and sequestration, heterogeneous catalysis and atmospheric  
32 aerosols. Experimental investigation of reactive and/or inelastic collisions of gas-phase species  
33 with liquid surfaces has lagged behind the equivalent with solid surfaces, generally because of the  
34 added difficulties of handling liquids in high-vacuum experiments. More recently, however,  
35 scattering at the gas-liquid (G-L) interface has been the subject of increasing experimental  
36 investigation.<sup>1-3</sup>  
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48 The majority of experimental studies of G-L scattering have used molecular beam sources to  
49 direct the incident atoms or molecules at the surface, ensuring a well-defined collision energy and  
50 incident angle, as well as a cold internal state distribution for incident molecules. Two main  
51 experimental approaches have been taken to detect the gas-phase products of scattering. Mass  
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3 spectrometric detection has the substantial advantage of ‘universality’, and is well suited through  
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5 time-of-flight measurements to the determination of product translational energy distributions, and  
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7 if implemented with rotation of the detector assembly, to measurement of angular scattering  
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9 distributions.<sup>1-5</sup> However, it does not provide resolution of the product quantum-state distribution.  
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11 The alternative approach, first demonstrated for inelastic scattering of I<sub>2</sub> by McCaffery and co-  
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13 workers,<sup>6-7</sup> and subsequently developed and extensively applied in our own laboratory,<sup>8-17</sup> and  
14  
15 separately by Nesbitt and co-workers,<sup>18-33</sup> is to use laser spectroscopic techniques. These are  
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17 inherently quantum state specific, but do not provide speed and angular information in such a  
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19 straightforward fashion.  
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24 Our previous work has used laser-induced fluorescence (LIF) to detect OH(D)(X<sup>2</sup>Π) radicals,  
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26 either as the reactive product of O(<sup>3</sup>P/<sup>1</sup>D) scattering at liquid surfaces containing alkyl groups, or  
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28 as the direct result of inelastic scattering of OH(D) from inert and reactive surfaces. This detection  
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30 technique has been coupled to both photolytic generation of the reactive O or OH directly above  
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32 (typically 10 mm) the liquid surface, and to molecular beam sources of OH(D).<sup>16</sup> With photolytic  
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34 and molecular beam sources of OH(D), we have determined reactive sticking coefficients for  
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36 OH(D) at saturated and unsaturated hydrocarbon surfaces, together with ro-vibrational product  
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38 state distributions for OH(D) inelastic scattering at reactive hydrocarbon and inert surfaces.<sup>9, 16, 34</sup>  
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40 Using photolytic generation we have studied reactions of O(<sup>3</sup>P) or O(<sup>1</sup>D) at saturated and  
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42 unsaturated hydrocarbon surfaces, determining ro-vibrational product state distributions as well as  
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44 information on the translational energy distributions of these products.<sup>8, 10, 12, 14</sup> We have used our  
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46 understanding of O(<sup>3</sup>P) reaction dynamics at hydrocarbon surfaces, arising from these dynamical  
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48 studies of reactive and inelastic scattering, to develop reactive atom scattering (RAS) as a probe  
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50 of the hydrocarbon density at the liquid surface, and have applied it to understanding the interfacial  
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3 chemical structure of a wide range of ionic liquids and ionic-liquid mixtures.<sup>11, 13, 15</sup> Most recently,  
4 we have extended this methodology to real-space LIF imaging, expanding the probe laser beam to  
5 a sheet intercepting both the in-going OH molecular beam, and out-going scattered OH. Imaging  
6 of the fluorescence in the plane containing the molecular beam and the surface normal as a function  
7 of time after the OH is incident on the surface provides a real-space measurement of the scattering  
8 dynamics for a single ro-vibrational state, enabling correlated angular and translational energy  
9 information to be determined.<sup>17</sup>

19 Nesbitt and co-workers have also used LIF to detect the products of inelastic scattering at G-L  
20 interfaces, specifically NO ( $X^2\Pi$ ) scattering from ionic liquids and liquid metals,<sup>28-30, 32</sup> and  
21 desorbing from an aqueous microjet.<sup>33</sup> More significantly for the work presented here, they have  
22 also demonstrated the application of direct high-resolution laser absorption spectroscopy in the  
23 mid-IR for the detection of the products of G-L scattering. In a wide range of experiments, this has  
24 included HF formed as a product of reactive scattering of F( $^2P$ ) at a saturated hydrocarbon  
25 surface,<sup>20, 25</sup> and extensive measurements of the dynamics of inelastic scattering, particularly of  
26 CO<sub>2</sub>, at a range of liquid surfaces.<sup>18-19, 21-24, 26-27</sup> Absorption spectroscopy is generally less sensitive  
27 than LIF, and enhancing sensitivity requires long path lengths, resulting in much lower spatial  
28 sensitivity than LIF. However, a fundamental advantage is the ability to probe many species that  
29 are inaccessible to LIF, because they lack suitable fluorescent excited electronic states. This is the  
30 case for many closed shell species, such as HF and CO<sub>2</sub>. In contrast, essentially all molecular  
31 species outside homonuclear diatomics exhibit vibrational transitions that are accessible via IR  
32 absorption spectroscopy. Another advantage of IR laser absorption spectroscopy is that it is  
33 conventionally performed with continuous wave (cw) lasers. When combined with pulsed  
34 generation of the incident atoms or molecules this enables a complete measurement of the  
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3 appearance time of the scattered products, and hence information on the translational energy of the  
4 scattered products, to be determined on every repetition. This results in a duty cycle improvement  
5 over conventional LIF with pulsed lasers, where the delay between generation and probing must  
6 be scanned in a sequential fashion. The narrow spectral bandwidth of most cw-lasers also allows  
7 high-resolution Doppler spectroscopy of individual ro-vibrational transitions, and the consequent  
8 measurement of the projection of the molecular velocity distribution onto the laser-propagation  
9 axis, which is generally perpendicular to the surface normal. Such Doppler spectroscopy is not  
10 easily achievable in LIF with conventional pulsed dye lasers, as their typical spectral bandwidths  
11 are similar to the measured Doppler widths.  
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24 In this paper, we demonstrate the first application of frequency-modulated (FM) transient  
25 absorption spectroscopy to gas-liquid scattering. FM absorption spectroscopy has been widely  
26 used as a sensitive spectroscopic method,<sup>35-36</sup> which has been applied previously to probe gas-  
27 phase photodissociation dynamics,<sup>37-38</sup> reaction kinetics,<sup>39-40</sup> and collisional energy transfer  
28 dynamics.<sup>41-42</sup> The first allowed electronic transition of the cyanogen radical,  $\text{CN}(A^2\Pi-X^2\Sigma^+)$ ,  
29 occurs in the near-infrared, convenient for many commercially available narrow-band continuous-  
30 wave laser sources. This makes it an excellent target species for transient FM spectroscopy. In our  
31 laboratory, we have previously applied FM spectroscopy to study the dynamics of gas-phase  
32 collisional energy transfer of both  $\text{CN}(X^2\Sigma^+)$  and  $\text{CN}(A^2\Pi)$  radicals.<sup>43-49</sup> In this paper, we combine  
33 the sensitive FM absorption detection with a new pulsed molecular beam source of  $\text{CN}(X)$  radicals  
34 to study the inelastic scattering of  $\text{CN}(X)$  at an inert perfluoropolyether (PFPE) liquid surface.  
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## EXPERIMENTAL METHODS

Experiments were performed in a newly constructed vacuum apparatus (Fig. 1), consisting of molecular beam source and liquid-surface scattering chambers, separated by a removable bulkhead. The source and scattering chambers were evacuated by turbomolecular pumps (Edwards nEXT400D and nEXT300D respectively), which were backed by a dry scroll pump (Edwards XDS 10iC), providing a base pressure of ca.  $10^{-8}$  mbar.

A molecular beam of CN(X) radicals was produced by a pulsed DC electric discharge of BrCN (Sigma-Aldrich 97%) diluted to a mole fraction of 0.4% in He carrier gas (BOC gases, CP grade 99.999%, total pressure 3 bar) at the exit of pulsed valve (Parker series 9, 1 mm aperture). We have previously described the design of the electric discharge system in application to production of an OH(X<sup>2</sup>Π) molecular beam.<sup>16</sup> The high voltage pulse, nominally a square wave with rise and fall times of  $\approx 10$  ns, was produced by a circuit based around a commercial push-pull fast switch (Behlke HTS-41-06-GSM). This was externally triggered to switch between ground and the optimized discharge voltage of -2000 V for a period of 10  $\mu$ s,  $\sim 100$   $\mu$ s into a gas pulse of nominal overall length 260  $\mu$ s. These timings were controlled by a digital delay generator (Stanford Research Systems DG535). The optimized voltage was established by monitoring both the CN FM signal size (vide infra) and the shot-to-shot stability of the discharge. The stability was improved by seeding with electrons emitted from a hot tungsten filament (Agar Scientific A054,  $I = 2.6$  A,  $V = 15 - 20$  V), positioned in the line of sight of the discharge,  $\sim 2$  cm in front and  $\sim 2$  cm to the side of the exit of the discharge.<sup>50</sup> Without the filament, discharge stability varied from day-to-day, with failure to strike on up to 30% of shots. With the filament consistent operation was achieved, with  $< 1\%$  of shots missed. Discharge stability was also found to improve at lower



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3 repetition rates of the pulsed valve, and a balance between this and the duty cycle resulted in the  
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5 selection of 5 Hz for the experiments presented here.  
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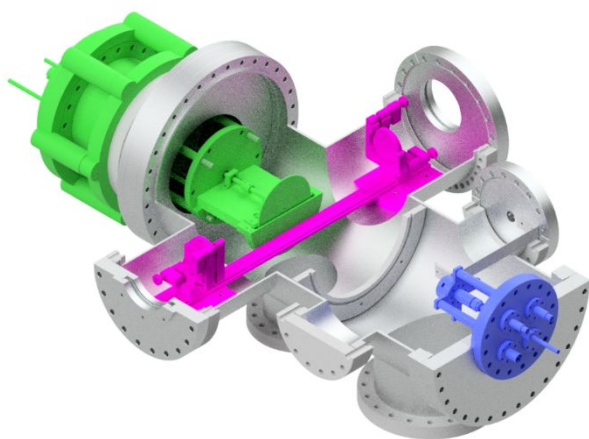
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9 The CN molecular beam was directed, parallel to the surface normal, at a continuously-refreshed  
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11 liquid surface, generated by the well-established rotating-wheel method.<sup>2-3</sup> The PFPE (Krytox  
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13 1506 (F-[CF(CF<sub>3</sub>)CF<sub>2</sub>O]<sub>14ave</sub>-CF<sub>2</sub>CF<sub>3</sub>), Dupont) was contained within a copper bath. The  
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15 temperature of the bath was controlled by a heater/chiller (Cole-Parmer Polystat WZ-12122-34)  
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17 with an operating range of -28 to 100°C. In the work presented here, all measurements were  
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19 performed at 25°C, where the vapor pressure of PFPE is  $\approx 10^{-7}$  mbar. A 10 cm diameter stainless-  
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21 steel wheel was partially submerged in the PFPE. The wheel rotated at 0.5 Hz and was  
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23 consequently coated in a continually refreshed layer of the liquid. The wheel-bath assembly was  
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25 mounted on a heavy-duty in-vacuum z-translator (LewVac M-HDZ101-160CF), enabling it to be  
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27 either positioned in line with the probe Herriott cell (vide infra) or retracted by 10 cm, to enable  
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29 measurements on the incident molecular beam without surface-scattering interference. The  
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31 molecular beam source was operated as a free-jet expansion, positioned 317 mm from the wheel,  
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33 and directed at a spot on the wheel 25 mm above the axis of rotation and horizontally centered.  
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35 The radius of the expansion at the surface was estimated from analysis of the Doppler lineshape  
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37 for  $j = 0.5$  to be  $\approx 100$  mm. Under operating conditions, with the PFPE and the molecular beam  
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39 present in the chamber, the average pressure was  $2-5 \times 10^{-5}$  mbar.  
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47 CN was probed using frequency-modulated transient absorption via R<sub>1</sub> branch lines of the A<sup>2</sup>Σ<sup>+</sup>-  
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49 X<sup>2</sup>Π (2,0) band between 778 and 795 nm. The FM probe system has been described in detail in  
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51 several previous publications, and only the essentials are presented here.<sup>43, 45, 48</sup> The output of a  
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53 single mode external-cavity tunable diode laser (Sacher GmbH TEC520) was frequency modulated  
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55 at 400 MHz using a broadband phase modulator (Quantum Technologies, TWAP-10). A  
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3 wavemeter (Angstrom WS-6) and a scanning Fabry-Perot interferometer were used to monitor the  
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5 frequency modulation and provide an accurate wavelength scale. The laser beam was multi-passed  
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7 parallel to the liquid surface in a Herriott cell located inside the vacuum chamber. The Herriott cell  
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9 was of the design of Kaur et al,<sup>51-52</sup> using mirrors (Thorlabs CM508-100-E03, reflectivity  $R \geq$   
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11 0.995 from 750 to 1100 nm, radius of curvature,  $r = 20$  cm) separated by 40.1 cm. The beams  
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13 converged on the center of the cell, forming a circle of  $\sim 8$  mm diameter with 14 passes that gave  
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15 a total path length within the Herriot cell of  $\approx 5.6$  m, at a nominal distance of 20 mm from the  
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17 surface of the wheel. The output was passed to a 1 GHz photoreceiver (NewFocus 1601FS-AC),  
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19 providing RF and DC signals. The RF signal was demodulated using an I & Q demodulator (Pulsar  
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21 Microwave, ID-10-412) to produce in-phase (I) and quadrature (Q) signals, which were low-pass  
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23 filtered (Minicircuits BLP-1.9+) and recorded by a digital storage oscilloscope (LeCroy, LT264,  
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25 350 MHz, 1 GSample s<sup>-1</sup>). In the experiments reported here, the total acquisition timebase was 500  
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27  $\mu$ s, with a time-step of 200 ns. The DC signal from the detector was also recorded by the  
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29 oscilloscope to provide a monitor of the laser power as a function of wavelength.  
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36 The experiment was controlled by custom written Labview software. The oscilloscope was used  
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38 to average the I and Q waveforms over 250 valve shots for each probe laser wavelength, which  
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40 was stepped across the transition in intervals of  $\sim 100$  MHz, with typically between 60 and 80  
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42 wavelength points recorded for each scan. Measurements were made in the following sequence, to  
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44 provide reliable relative signal sizes for different rotational states measured on different days. First,  
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46 a measurement of the incident molecular beam only was made, probing  $j = 0.5$  via the  $R_1(0.5)$   
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48 transition with the wheel/bath assembly retracted from the probe region. For selected rotational  
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50 states in the range  $j = 4.5$  to 14.5 separate measurements were then made with the wheel/bath  
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52 assembly both retracted from, and inserted into, the probe region. The order in which these ‘wheel  
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3 out' and 'wheel in' measurements were made was alternated, and different final states were  
4 measured in a random sequence. The 'wheel out' measurements provided a background  
5 measurement of the small amount of CN present in the molecular beam in these higher rotational  
6 states. No significant population was observed in the molecular beam for  $j \geq 14.5$ , and for these  
7 states only the 'wheel in' or scattering measurements were made. After each pair of scattering and  
8 background measurements were made, the wheel/bath assembly was retracted again and the cycle  
9 restarted with another measurement of the incident beam  $j = 0.5$  state. To ensure that scattering  
10 only came from the coated region of the wheel, and not from the bath surface, additional  
11 measurements were made with the wheel/bath assembly inserted, but with the wheel itself  
12 removed. No measurable scattering was observed with this arrangement, providing confidence that  
13 the scattering observed arises solely from the presence of the liquid-coated wheel.  
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46 **Figure 1.** A schematic representation of the experimental apparatus, with the DC electric discharge  
47 molecular beam source in blue, the rotating wheel liquid surface assembly in green, and the in-  
48 vacuum Herriott cell in magenta.  
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## DATA ANALYSIS

The data consisted of I and Q signals as a function of time after the HV discharge trigger, together with the average probe laser power, for each wavelength. The first step in the data analysis was rotation of the I and Q signals by the overall experimental phase angle, to yield absorption (A) and dispersion (D) signals. The phase angle was determined independently using the well-established self-consistent methodology of North and Hall.<sup>36</sup> The A and D signals were then normalized at each wavelength by the average probe laser power. The x-axis was linearized in frequency using the simultaneously acquired monitor-etalon information, converted to Doppler shift in  $\text{ms}^{-1}$ . The line center was determined by finding the positions of the positive and negative peaks of the FM absorption signal, from a line shape averaged over the entire observed signal time, with the x-axis truncated to  $\pm 2000 \text{ ms}^{-1}$ . When processing both scattering and background measurements, FM Doppler line shapes for sequential  $2 \mu\text{s}$  averages of the A and D signals were then constructed, with the baseline established using a pre-signal gate. The A and D FM Doppler lineshapes were simultaneously fitted, to determine the speed distribution of the CN radicals along the probe laser beam propagation direction, and thereby perpendicular to the molecular-beam axis and surface normal. The fitting process has been previously described in detail, with an assumed speed distribution used to simulate FM absorption and dispersion line shapes, including the appropriate linestrength for the probe transition. A simplex minimization was then applied to find the best fit speed distribution.<sup>43, 45</sup> The integral of the speed distribution for each  $2 \mu\text{s}$  average was then used to determine the relative population as a function of delay, which we refer to as an appearance profile. The measurements of the incident molecular beam via the  $j = 0.5$  state were averaged over the entire delay for which signal was observed, from 130 to 250  $\mu\text{s}$ . The single resulting A and D profiles were fitted as described above and integrated to yield a single number

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3 quantifying the incident beam population. The average of incident-beam measurements made  
4 immediately before and after the scattering and background measurements was used to normalize  
5 these to day-to-day fluctuations in the performance of the CN-radical-discharge source.  
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## 14 RESULTS

### 15 16 17 18 **A. Characterization of incident $\text{CN}(X^2\Sigma^+)$ molecular beam**

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21 Molecular-beam sources of  $\text{CN}(X^2\Sigma^+)$  have been reported previously, and have been  
22 subsequently applied to crossed molecular-beam scattering dynamics experiments. These sources  
23 have used either photodissociation of a suitable precursor (e.g.  $\text{BrCN}$  or  $\text{C}_2\text{N}_2$ ),<sup>53-54</sup> or  
24 photoablation of a graphite rod to form C atoms followed by reaction with  $\text{N}_2$ ,<sup>55</sup> to generate CN  
25 radicals that were subsequently entrained and cooled in a supersonic expansion to form a molecular  
26 beam. To the best of our knowledge, there are no previous reports of the use of a DC electric  
27 discharge to generate the CN radicals for subsequent entrainment and cooling.  
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38 Figure 2(a) shows appearance profiles for CN rotational states in the range  $j = 0.5$  to 14.5, with  
39 the relative signal sizes directly reflecting the relative populations in the different states, where the  
40 error bars are  $1\sigma$  standard error of the mean from 3 independent measurements. In each case, the  
41 signal rises rapidly to a peak, before decaying more slowly to zero. The 10% to 90% rise time for  
42  $j = 0.5$  is 7  $\mu\text{s}$ , comparable to the 10  $\mu\text{s}$  discharge pulse length, supporting the idea that this (as  
43 expected) reflects the on-axis leading edge of the CN packet intersecting the probe laser. The  
44 falling edge is slower, and for  $j = 0.5$  displays a clear shoulder at  $\approx 175 - 185 \mu\text{s}$ . Since the  
45 molecular beam is not skimmed, we cannot directly convert the appearance profile into an on-axis  
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3 speed distribution, as the shape of the falling edge will be a convolution of the speed distribution  
4 with the angular spread of the molecular beam. Doppler lineshapes recorded at different delays  
5 can be fitted to determine the transverse speed distributions, which indicate variations in the  
6 angular distribution in the expansion associated with the observed shoulder in the appearance  
7 profile (see Supporting Information). The time at which the peak signal appears after the discharge  
8 pulse, 156  $\mu\text{s}$ , corresponds to a CN speed of  $1.90 \times 10^3 \text{ ms}^{-1}$ . This is faster than the thermodynamic  
9 prediction for a 100% He expansion from a room-temperature reservoir (ca.  $1.75 \times 10^3 \text{ ms}^{-1}$ ). In  
10 experiments using an identical discharge source that generated OD from the dissociation of  $\text{D}_2\text{O}$   
11 seeded in He, we measured an OD molecular beam speed of  $1.81 \times 10^3 \text{ ms}^{-1}$ .<sup>16</sup> It therefore appears  
12 that the molecular beams generated from discharge sources of this design are modestly faster than  
13 conventional molecular beams from room-temperature reservoirs, consistent with additional  
14 heating of the source gas within the discharge volume by the applied current. Considering the  
15 entire appearance profile, the average kinetic energy of the CN molecular beam along the surface  
16 normal is  $43.5 \text{ kJ mol}^{-1}$ . The total populations in different rotational levels in the  $f_1$  spin-rotation  
17 manifold, relative to the population of the  $j = 0.5$  level, are shown in Figure 2(b). The lowest  
18 rotational level,  $j = 0.5$ , is the most populated level, with a steady decline in population with  
19 increasing  $j$ , indicating that a substantial degree of rotational cooling has occurred in the post-  
20 discharge expansion. The distribution does not fit to a single rotational temperature, but does fit  
21 well to a weighted 2-temperature distribution (Equation 1), shown as a logarithmic plot in the inset  
22 to Figure 2(b).  
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$$\frac{P(j)}{(2j+1)} = C \left[ \left( \frac{\alpha}{T_1} \right) e^{-\frac{E_{\text{rot}}(j)}{k_B T_1}} + \left( \frac{1-\alpha}{T_2} \right) e^{-\frac{E_{\text{rot}}(j)}{k_B T_2}} \right] \quad (1)$$

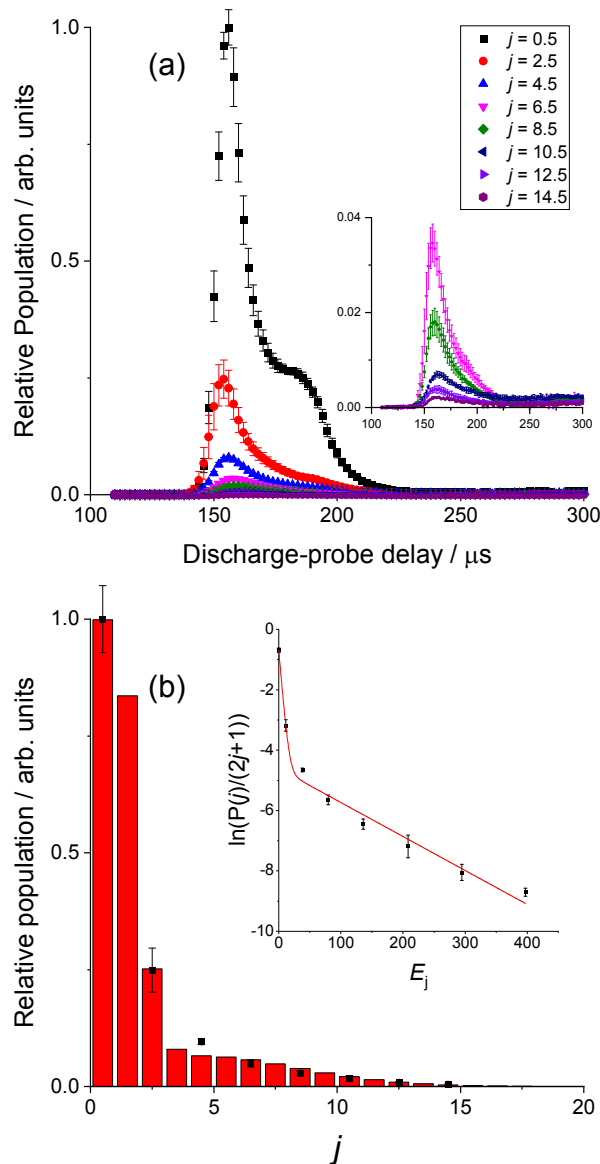
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Here  $P(j)$  is the relative population of level  $j$ , with rotational energy  $E_{\text{rot}}(j)$ ,  $T_1$  and  $T_2$  are the rotational temperatures,  $\alpha$  is the fraction at temperature  $T_1$ , and  $C$  is an arbitrary overall scaling parameter. The results of this fit are displayed in Table 1, demonstrating that the majority of the rotational distribution is well described by a  $< 10$  K temperature, with a minor component that is warmer, but still substantially below room temperature.

**Table 1.** Values of  $T_1$ ,  $T_2$  and  $\alpha$  obtained in a 2-temperature Boltzmann fit to the incident beam rotational populations. Confidence intervals are  $1\sigma$  standard errors.

$T_1 / \text{K}$	$T_2 / \text{K}$	$\alpha$
$6.0 \pm 0.8$	$127 \pm 13$	$0.70 \pm 0.05$

This confirms that the DC electric discharge demonstrated here produces a rotationally cold supersonic molecular beam of CN(X) radicals, without the additional expense and experimental complexity required by the introduction of a photolysis or ablation laser.



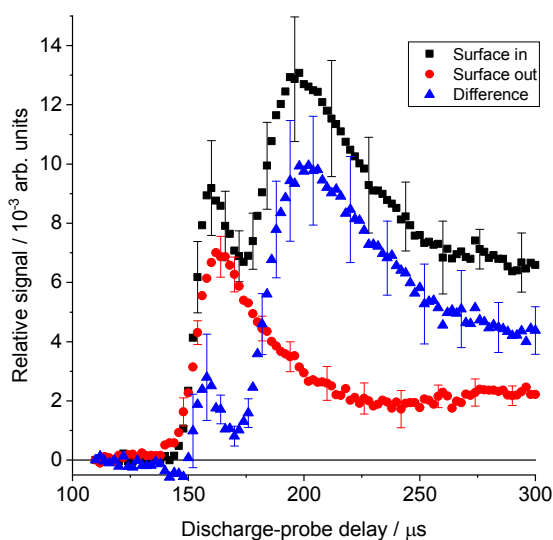
**Figure 2.** (a) Appearance profiles for the incident molecular beam for selected CN rotational levels,  $j = 0.5$  to  $14.5$ . (Inset) Expanded y-axis version of (a) showing appearance profiles for  $j = 6.5$  to  $14.5$ . (b) Relative rotational populations for selected rotational levels,  $j = 0.5$  to  $14.5$ , in the molecular beam. Experimental (black squares) and rotational distribution from the 2-temperature fit (red bars). (Inset) Two-temperature logarithmic fit of Equation 1 to the rotational populations in (b) to extract  $T_1$ ,  $T_2$  and  $\alpha$  as presented in Table 1.



## B. Inelastic Scattering of $\text{CN}(X^2\Sigma^+)$ from a PFPE Surface

Figure 3 presents appearance profiles for  $j = 10.5$ , chosen as a representative sample from the complete data set, recorded with both the liquid surface present and with the surface retracted, and the difference of the two. In each case, the appearance profile is the average of three independent measurements acquired on different days, with normalization to the incident CN molecular beam population as discussed in the data analysis section above. A small signal is observed for the incident beam with the liquid surface retracted, peaking at 160  $\mu\text{s}$  discharge-probe delay. This signal reaches a minimum at around 240  $\mu\text{s}$ , and remains essentially constant until the end of the acquired time period (300  $\mu\text{s}$ ), consistent with off-axis paths observed in the free-jet expansion for this low-population rotationally excited state. When the liquid surface is introduced, a slightly larger initial peak at 160  $\mu\text{s}$  is observed, followed by a local minimum, and then at  $\approx 200 \mu\text{s}$  by an even larger signal, which then decays at long times. The early peak cannot be the result of direct scattering of CN from the liquid surface, as there is insufficient time for the CN to reach the surface and rebound to the probe region, resulting in an  $\approx 40 \text{ mm}$  round trip. We believe that the increased early-time signal with the surface present is the result of gas-phase scattering. A relatively short temporal packet of CN radicals ( $\approx 20 \mu\text{s}$  full width at half maximum) is embedded within a longer ( $\approx 250 \mu\text{s}$ ) gas pulse. There is therefore time for the leading edge of the gas pulse, which is of course overwhelmingly composed of He, to strike the liquid surface and rebound into the path of the CN packet. Inelastic scattering with small positive  $\Delta j$  can then transfer some population from the highly populated low- $j$  ( $\leq 4.5$ ) levels up into the intermediate-to-high- $j$  levels. We have observed similar behavior in previous interfacial scattering experiments in our laboratory involving OH radicals generated in a pulsed DC discharge.<sup>16</sup> Consistent with this explanation, the

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3  $j \leq 4.5$  levels display a negative difference around this time delay, while higher levels display  
4 successively smaller early peaks. Previous studies of gas-phase inelastic scattering of  $\text{CN}(X^2\Sigma^+)$   
5 with He are also consistent with this picture, in which small  $\Delta j$  transfers are associated with strong  
6 forward scattering and low translational energy transfer, maintaining the incident molecular beam  
7 speed while redistributing some of the population across low- $j$  levels.<sup>43</sup> We minimized this effect  
8 by triggering the discharge as early as possible within the molecular beam pulse while still  
9 maintaining discharge stability, as well as optimizing the valve-surface distance and consequent  
10 molecular-beam density at the liquid surface.  
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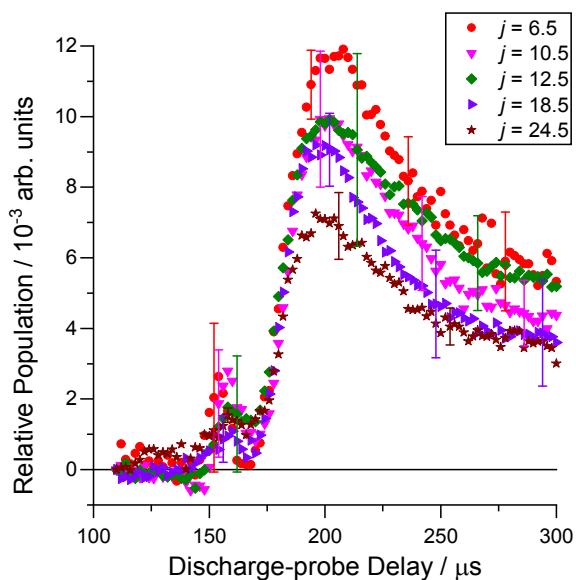


44 **Figure 3.** Appearance profiles for  $j = 10.5$ , with the liquid surface retracted (red circles) and  
45 inserted (black squares), and the difference of these (blue triangles). Error bars represent  $1\sigma$   
46 standard error of the mean of three independent measurements.  
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51 The large secondary peak, centered around  $200 \mu\text{s}$ , is only present when the surface is inserted,  
52 and is consistent with a returning wave of CN radicals that have undergone inelastic scattering at  
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3 the liquid surface reaching the probe region. This returning signal can, of course, be larger than  
4 the incident molecular beam signal for this rotational level as a consequence of translation to  
5 the incident molecular beam signal for this rotational level as a consequence of translation to  
6 rotational energy transfer at the liquid surface populating this level from the more highly populated  
7 low- $j$  levels in the incident beam. This observation and its interpretation is consistent with our  
8 previous inelastic scattering experiments using LIF probing.<sup>9, 16-17, 34</sup>  
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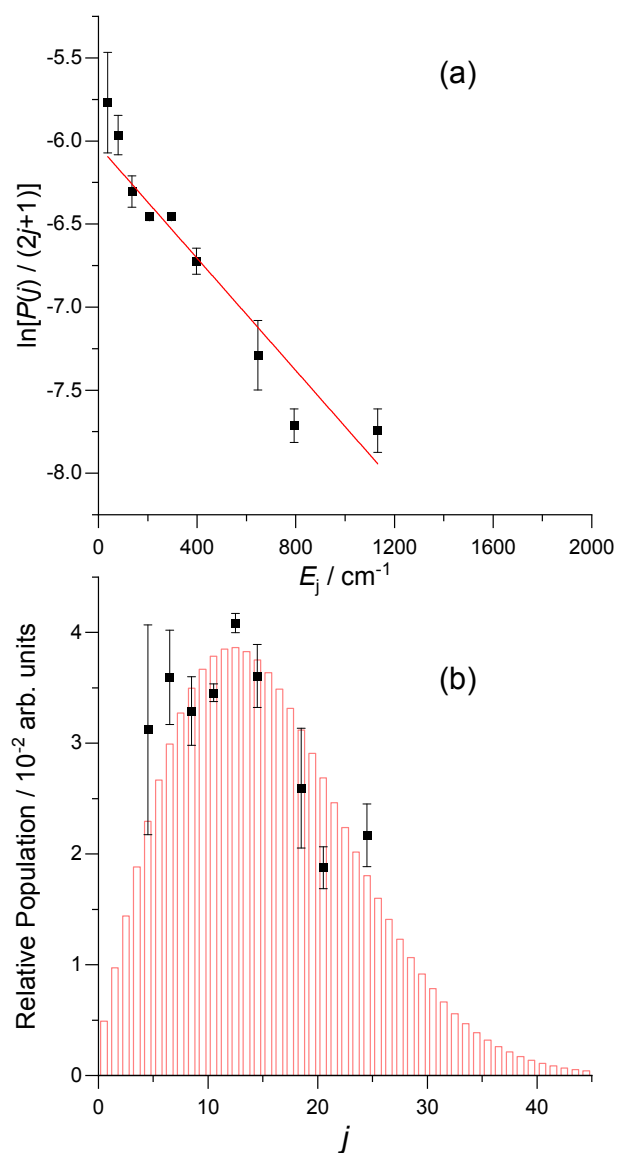
16 In Figure 4 we show appearance profiles for selected final states in the  $f_1$  spin-rotation manifold,  
17  $j = 6.5, 10.5, 12.5, 18.5,$  and  $24.5$ , relative to the population of the incident  $j = 0.5$  level shown in  
18 Figure 2(a). For  $j = 6.5$  to  $12.5$ , these are differences of surface present and surface retracted,  
19 however for  $j = 18.5$  and  $24.5$  the incident beam intensity was negligible, and only the surface  
20 present signal is presented. Clear differences in the overall signal sizes are observed, consistent  
21 with varying rotational populations in the different final states. The rising edges of the appearance  
22 profiles, and the peak times, are very similar for all final states. Differences are observed in the  
23 falling edge of the profiles, although no clear trend with final- $j$  is apparent.  
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3 **Figure 4.** Appearance profiles for CN( $X^2\Sigma^+$ ) inelastically scattered from PFPE, for selected final  
4 rotational levels,  $j$ . Populations are relative to that from the incident  $j = 0.5$  level. Selected error  
5 bars are 1 standard error of the mean of 3 independent measurements on different days. For  $j \leq$   
6 12.5 the profile is the difference of surface present and retracted, for  $j = 18.5$  and 24.5 the profile  
7 is surface present only.  
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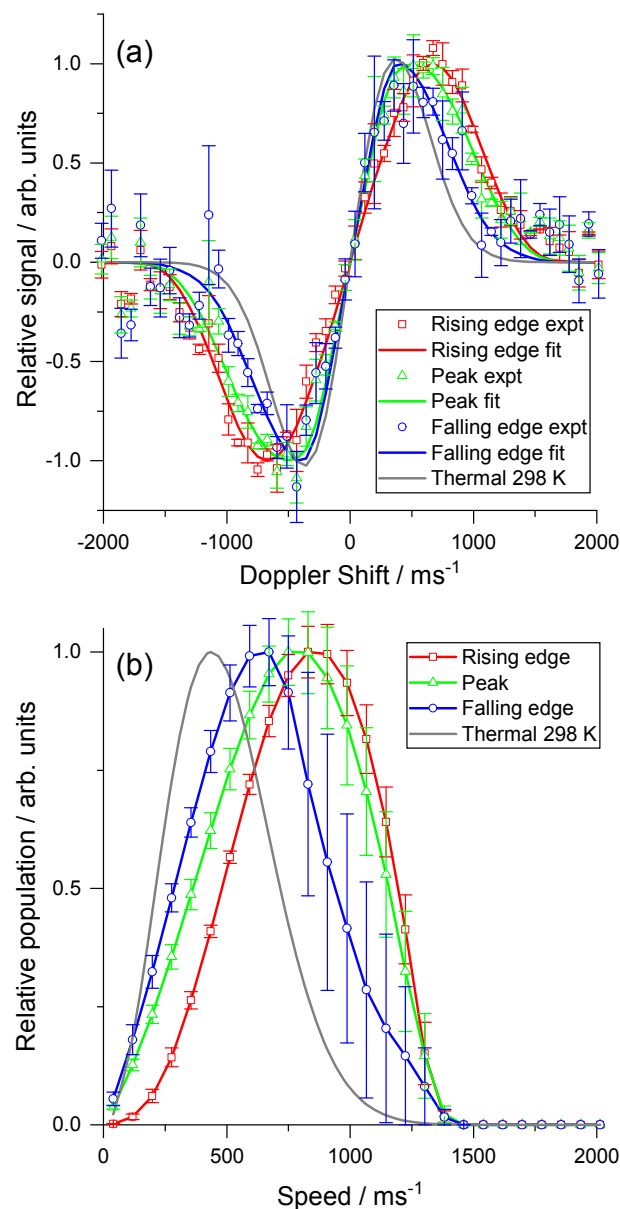
15 The relative rotational populations derived from integrating the appearance profiles in the delay  
16 range 176 – 266  $\mu\text{s}$  are shown in Figure 5. We have excluded signals after 266  $\mu\text{s}$  to ensure that  
17 the rotational populations are not modified by secondary gas-phase collisions. It is difficult to  
18 determine the pressure in the probe region at the experimental measurement time. A typical  
19 centerline pressure for a pulsed molecular beam is of order 1 mTorr. Assuming a gas kinetic rate  
20 constant typical for rotational energy transfer ( $10^7 \text{ Torr}^{-1} \text{ s}^{-1}$ ), at this pressure the CN would  
21 undergo a collision every 100  $\mu\text{s}$ . However, the surface-scattered CN and He are expanding into  
22 an evacuated chamber ( $1 \times 10^{-5} \text{ mbar}$ ), implying that the average probe region pressure is  
23 substantially less than 1 mTorr during this experimental measurement time, and that accordingly  
24 the nascent rotational distributions from surface scattering are not substantially modified by  
25 subsequent gas-phase collisions. We note that in principle the signals should be corrected for flux-  
26 density effects, as the absorption probe method measures the instantaneous density in the probe  
27 beam, which necessarily depends on the speed of the scattered CN. However, as in our previous  
28 experiments studying OH inelastic collisions using LIF, providing an appropriate correction to  
29 convert this density to a flux is challenging, given the unknown details of the scattering angle  
30 distribution and its interaction with the (multi-beam) probe laser geometry.<sup>16</sup> Given the similar  
31 shapes of the appearance profiles in the integrated time-window, we have assumed that the  
32 appropriate density-flux correction will have similar effects on the different rotational levels, and  
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3 accordingly present rotational populations without correction. Figure 5(a) displays a Boltzmann  
4 plot of the rotational populations and the associated linear fit which yields a rotational temperature,  
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6  $T_R = 850 \pm 130$  K. No significant improvement in the quality of the fit was found when fitting to  
7  
8 a two-temperature model, as given by Equation 1. Figure 5(b) shows the relative rotational  
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10 populations as a function of  $j$ , together with a simulation for  $T_R = 850$  K normalized to have the  
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12 same total population among the observed levels.  
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**Figure 5.** (a) Boltzmann plot for  $\text{CN}(X^2\Sigma^+)$  scattered from the PFPE surface, spanning rotational levels in the  $f_1$  spin-rotation manifold ranging from  $j = 4.5$  to  $j = 24.5$ , together with the linear best fit. Error bars are  $1\sigma$  standard error of the mean from 3 independent measurements. (b) Rotational populations, relative to that for the incident  $j = 0.5$  level. Experiment (black squares), simulation assuming  $T_R = 850$  K from the linear fit in (a) (red bars).

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3 Figure 6(a) shows FM Doppler absorption lineshapes for CN inelastically scattered into  $j = 6.5$ ,  
4 summed over three selected time periods which we define as: rising edge (176 – 191.8  $\mu\text{s}$ ); peak  
5 (192 – 223.8  $\mu\text{s}$ ); and falling edge (224 - 266  $\mu\text{s}$ ). The results of fitting to extract the speed  
6 distribution are shown, as well as a simulation of a 298 K Gaussian Doppler lineshape, appropriate  
7 for a thermalized gas-phase velocity distribution. All three scattered Doppler lineshapes are  
8 significantly wider than the thermal lineshape, indicating translational temperatures perpendicular  
9 to the surface that are greater than 298 K. The width of the lineshapes clearly decreases from the  
10 rising edge to the falling edge, demonstrating that the early-appearance-time CN has a higher  
11 transverse translational energy. This trend is reproduced for all final product states probed (see the  
12 Supporting Information). The transverse speed distributions for these different delays, extracted  
13 from the fits in Figure 6(a), are presented in Figure 6(b), together with a Maxwell-Boltzmann  
14 distribution for 298 K. Consistent with the observed Doppler lineshapes, the transverse speed  
15 distributions for all of the measured delays peak at substantially higher speeds than the 298 K  
16 Maxwell-Boltzmann distribution, with most probable speeds of 830, 750 and 670  $\text{ms}^{-1}$  for the  
17 rising edge, peak and falling edge delays, respectively, while the most probable speed for the 298  
18 K Maxwell-Boltzmann is 436  $\text{ms}^{-1}$ . The shapes of the fitted transverse speed distributions are also  
19 inconsistent with Maxwell-Boltzmann distributions, a feature particularly noticeable for the rising-  
20 edge delay, where the transverse speed distribution displays sharper curvature on the fast side than  
21 the slow, i.e. the opposite of a Maxwell-Boltzmann. This non-Boltzmann behavior is directly  
22 reflected in the observed Doppler lineshapes, and attempts to fit these to Gaussian lineshapes (the  
23 one-dimensional Doppler projection of a Maxwell-Boltzmann distribution) varying the  
24 translational temperature were unsuccessful, confirming that the lineshapes are significantly non-  
25 Gaussian.  
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**Figure 6.** (a) FM absorption Doppler lineshapes for  $j = 6.5$ , integrated over rising edge, peak and falling edge delays. Rising edge data (red open squares) and fit to determine the translational energy distribution (red solid line), peak data (green open triangles) and fit (green solid line), falling edge data (blue open circles) and fit (blue solid line). Simulation of FM Doppler lineshape for 298 K Maxwell-Boltzmann speed distribution (grey solid line). (b) Speed distributions extracted from the fits to data shown in (a). Rising edge (red squares and line), peak (green



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3 triangles and line), falling edge (blue circles and line) and a 298 K Maxwell-Boltzmann  
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5 distribution (grey line).  
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## 10 **DISCUSSION**

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12 We first discuss the measured rotational distribution for the scattered CN. It is immediately  
13 obvious that the scattered CN is rotationally excited relative to the incident molecular beam  
14 distribution. The scattered distribution is reasonably well-described by a Boltzmann distribution  
15 with a temperature,  $T_R = 850$  K, which is substantially above that of the surface,  $T_S = 298$  K. It is  
16 very common in surface-scattering experiments to analyze the observed scattering by comparison  
17 to two limiting cases. The first is *thermal desorption* (TD), where the incident species has fully  
18 accommodated with the surface before desorption. A TD sample will therefore display a rotational  
19 distribution reflecting the surface temperature, as well as a Maxwell-Boltzmann speed distribution  
20 similarly defined by  $T_S$ . The dramatically higher rotational temperature observed here suggests  
21 that there is at most a modest component of TD scattering in this system. By definition, the  
22 remaining fraction of the scattering that is not TD is described as *impulsive scattering* (IS), in  
23 which the incident species has undergone one or potentially a small number of collisions with the  
24 surface, but has not fully equilibrated with it. There is no *a priori* reason why the rotational  
25 distribution from a direct scattering process should be described by a rotational temperature, but  
26 recent experiments studying a range of molecular species with a wide variety of liquid surfaces  
27 have shown that this is a very common outcome.<sup>9, 16-19, 21-22, 24, 27-31, 34, 56</sup> The fitted rotational  
28 temperature corresponds to a fraction  $f_R = 0.16 \pm 0.02$  of the available incident kinetic energy being  
29 converted from translation to rotation in collisions at the liquid surface. This is broadly comparable  
30 to the previous limited measurements of rotationally inelastic scattering of small molecules at  
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3 PFPE surfaces. In our own previous work using LIF to study OD inelastic scattering at a PFPE  
4 surface, using a molecular beam source at normal incidence and a laboratory frame kinetic energy  
5 of 30 kJ mol<sup>-1</sup>, we found  $f_R = 0.11$ .<sup>16</sup> Nesbitt and co-workers have studied both CO<sub>2</sub> and NO  
6 collisions with PFPE. In both cases, the product rotational distributions can be fitted to a two-  
7 temperature IS:TD model. Considering the IS components alone,  $f_R = 0.14$  and 0.12 for CO<sub>2</sub> and  
8 NO, respectively, at incident kinetic energies of 44 and 84 kJ mol<sup>-1</sup>.<sup>22, 31</sup> In contrast to the work of  
9 Nesbitt and co-workers, but consistent with our own previous work on OH inelastic scattering, we  
10 see no strong evidence for a TD component in the rotational distribution within the limitations of  
11 the measured signal-to-noise ratio, and therefore conclude that the rotational distribution is  
12 dominated by impulsive scattering.  
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26 We now consider the translational energy of the scattered CN. There are two sources of  
27 information for this: the shapes of the appearance profiles and the Doppler lineshapes. The delay  
28 between the peaks of the incident CN and scattered CN appearance profiles is essentially  
29 independent of the final rotational state at  $\approx 40 \mu\text{s}$ . The probe beams are centered 20 mm from the  
30 liquid surface, and the measured incident beam speed of  $1.9 \times 10^3 \text{ ms}^{-1}$  implies a flight time of  $\approx$   
31  $10 \mu\text{s}$  to the surface. The remaining  $\approx 30 \mu\text{s}$  delay is consistent with a scattered speed at the peak  
32 of the return signal of  $\approx 650 \text{ ms}^{-1}$ . This is faster than the most probable speed for a 298 K thermal  
33 distribution,  $436 \text{ ms}^{-1}$ , consistent with the general conclusion from the rotational distribution that  
34 the majority of the scattering is impulsive in nature. At face value, this corresponds to an  
35 approximate translational temperature of  $\approx 670 \text{ K}$ , comparable to but somewhat lower than the  
36 rotational temperature. However, caution should be exercised in relating the appearance profiles  
37 quantitatively to the scattered speed distribution in such a simple way. The return flight path, and  
38 hence return time-of-flight, is short compared to the incident packet width. This results in the  
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3 scattered appearance profile being strongly convoluted by the incident packet width. The probe  
4 region is also  $\approx 8$  mm in diameter, a significant fraction of the average 20 mm flight path from the  
5 surface. Most importantly, the scattered CN may be detected anywhere along any of the 14 probe  
6 beam paths in the Herriott cell, including locations which are some distance from the central axis  
7 of the incident molecular beam along the direction of laser-beam propagation. The actual flight  
8 paths from the surface to the probe beam that contribute to the observed appearance profile will  
9 therefore sample a wide range of product scattering angles, arising from collisions with the liquid  
10 surface across the width of the wheel upon which the initial CN beam was incident. There is no  
11 simple way to deconvolute these various effects. Monte-Carlo simulation can, in principle, be used  
12 to forward-simulate appearance profiles based on assumed scattering distributions, as  
13 demonstrated in some of our previous work using LIF as a probe method, although we have not  
14 attempted that yet here.<sup>9, 16</sup>

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17 More straightforwardly, the transverse Doppler lineshapes do provide unambiguous information  
18 on a component of the scattered CN velocities. The transverse speed distributions extracted from  
19 the lineshapes provide clear evidence of impulsive scattering, being substantially faster than a 298  
20 K thermal distribution. The most probable transverse speeds are 830, 750 and 670  $\text{ms}^{-1}$  for the  
21 rising edge, peak and falling edge delays, corresponding to average kinetic energies of 10.2, 8.8,  
22 and 6.7  $\text{kJ mol}^{-1}$ , respectively. This variation within the appearance profile is self-consistent with  
23 the speeds normal and transverse to the surface being correlated, and the simplest interpretation of  
24 the appearance profile as a (somewhat convoluted) time-of-flight measurement. Interestingly, no  
25 strong evidence for a substantial thermalized component of transverse speeds is observed even for  
26 the lower rotational levels, where it would be expected to make the largest contribution. It might  
27 hypothetically be possible to associate the slower transverse speeds with a TD component and the

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3 residual with an IS mechanism, but with no observable bimodality in the speed distribution there  
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5 is no clear justification for attempting such an analysis. This is consistent with what we have  
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7 concluded above about the absence of a substantial TD component in the rotational distributions,  
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9 within the current signal-to-noise level and finite number of probed rotational levels.  
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12 We have previously observed broadly similar behavior in inelastic scattering of OD from PFPE  
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14 surfaces, with scattered OD speeds that are superthermal and do not display any clear surface-  
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16 temperature thermal component.<sup>17</sup> In contrast, the scattered speed distributions of both NO and  
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18 CO<sub>2</sub> from PFPE observed by Nesbitt and co-workers have been successfully interpreted within an  
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20 IS:TD model, with substantial thermal components at the surface temperature, consistent with their  
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22 associated rotational temperature analysis.<sup>18-19, 21-22, 24, 27, 31</sup> The origin of these implied differences  
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24 in the fraction of the scattered distribution that appears to be surface equilibrated is as yet unknown.  
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26 Further work is clearly required, including improvements in signal-to-noise and an expansion of  
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28 the present study to include different incident kinetic energies, better-defined initial transverse  
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30 velocity distributions through skimming of the molecular beam, and the introduction of different  
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32 liquid surfaces, particularly potentially reactive hydrocarbon surfaces such as squalane, C<sub>30</sub>H<sub>62</sub>.  
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## 40 CONCLUSION

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42 We have reported the first application of frequency-modulation absorption spectroscopy as a  
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44 probe of gas-liquid interfacial scattering, including the first use of a DC electric discharge source  
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46 to generate a pulsed rotationally cold molecular beam of CN radicals. The rotationally inelastic  
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48 scattering of CN radicals at the surface of PFPE is dominated by impulsive scattering, as concluded  
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50 both from the extended rotational distributions and the non-Gaussian, superthermal transverse-  
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52 speed distributions. There is no clear evidence, within the current signal-to-noise, of bimodality in  
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3 either of these distributions and hence no need to invoke a discrete thermalized component to  
4 explain the observations. Overall, around 15% of the incident kinetic energy is converted into  
5 rotation, comparable amounts into translation, with the remainder lost into the (unobserved)  
6 motions of the PFPE. This study demonstrates the utility of FM-absorption spectroscopy as a  
7 sensitive probe of gas-liquid interfacial scattering, and extends the (limited) range of molecular  
8 species for which quantum-state resolved scattering information at liquid surfaces is available.  
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## 21 ASSOCIATED CONTENT

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23 **Supporting Information.** Figure S1 showing Doppler lineshapes as a function of discharge-  
24 probe delay for the incident molecular beam, and resulting transverse speed distributions. Figure  
25 S2 showing Doppler lineshapes for rising edge, peak and falling edge delays for three  
26 representative rotational levels  $j = 6.5, 12.5$  and  $18.5$ .  
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## 34 AUTHOR INFORMATION

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### 42 43 **Notes**

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45 The authors declare no competing financial interest.  
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## 48 49 **ACKNOWLEDGMENT**

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53 (University of Bristol) for helpful discussions.  
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