Infrared Spectrum of CH₃CN–HCl in Solid Neon, and Modeling Matrix Effects in CH₃CN–HCl and H₃N–HCl

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ABSTRACT:

Several IR bands for two isotopic forms of the $\text{CH}_3\text{CN-HCl}$ complex have been measured in neon matrices at 6 K. Assigned bands for the primary isotopomer include the ν_{CC} band at 926 cm^{-1} , ν_{HCl} the band at 2677 cm^{-1} , and the ν_{CN} band, which occurs as a doublet at $2308/2279\text{ cm}^{-1}$. The observed frequencies are reasonably consistent with previous observations in solid argon and/or nitrogen, with the exception of ν_{HCl} bands, which differed, and were ultimately found to shift systematically across various condensed-phase media. A plot of medium-induced shifts for the ν_{HCl} band vs. polarizability of the host substances is essentially continuous; except for the N_2 -matrix frequency, for which the shift is considerably larger than that expected on this basis. In an effort to clarify the physical underpinnings of these shifts, and their structural implications, a computational study was undertaken, which examined $\text{CH}_3\text{CN-HCl}$ as well as $\text{H}_3\text{N-HCl}$; a system for which analogous frequency shifts have been observed and characterized previously. Beyond equilibrium structure and frequency calculations, which predict that the ammonia complexes is stronger and undergoes a greater degree of structural change in bulk, condensed-phase media, the N-Cl potentials of both complexes were mapped in the gas-phase and in bulk, dielectric media. The predicted medium effects on these potentials are consistent with observations. The $\text{CH}_3\text{CN-HCl}$ curves shift slightly in response to the medium, consistent with a subtle enhancement of the hydrogen bond, and relatively small frequency shifts. The effects of the dielectric media on $\text{H}_3\text{N-HCl}$ are more substantial, and indicate significant degree of proton transfer, even for low-dielectric environments, which is constant with the extreme spectral shifts noted previously for this system.

Introduction

Hydrogen bonding has been studied for many decades, and infrared spectroscopy has been one of the primary tools for investigating hydrogen-bonded systems throughout [1-3]. In fact, some of the earliest matrix-isolation studies involved the characterization of small hydrogen-bonded clusters via infrared spectroscopy [3-5]. Still today, interaction energies of hydrogen-bonded complexes provide valuable benchmarks for the validation and testing of new quantum-chemical methodologies [6]. These systems, comprised of a “donor” subunit (HA) and an “acceptor” subunit (:B) in the most general sense, are often grouped into three classes. At one extreme are “Type I” complexes [3], which are weak, essentially non-bonded complexes, for which the interaction energies are typically 5 kcal/mol or less [2]. Nonetheless, a slight lengthening of the A-H bond does occur, and furthermore, the force constant is reduced, which produces the characteristic shift in the A-H stretching band that parallels the H-bond strength [1, 2]. Proton transfer lies at the opposite extreme, as in so-called “Type III” complexes [3], where the interaction between the donor and acceptor is particularly strong, and the bonding is best described as an ion-pair (A^-/HB^+)[7]. Intermediate between these extremes are “Type II” complexes [3], with “proton-shared” H-bonds ($A\cdots H\cdots B$) [2, 7], in which the proton is, to some extent, partially bonded to both A and B. The interaction energies in these latter two classes of systems can exceed 30 kcal/mol [2].

The amine-hydrogen halide complexes provide an example relevant to this study in which this entire range of interactions is nearly spanned by a single class of systems [7]. The strengths of these complexes and the extent of proton transfer vary systematically with the halogen and amine

substituents. A greater degree of proton transfer is observed as methylation of the amine is increased (*i.e.*, $(\text{CH}_3)_3\text{N} > \text{NH}_3$), and with larger halogens (*i.e.*, $\text{HBr} > \text{HF}$). As such, $\text{H}_3\text{N}-\text{HF}$ lies near one extreme as a purely hydrogen-bonded complex, though fairly strong. Near the other extreme is $(\text{CH}_3)_3\text{N}-\text{HBr}$, which is essentially an ion-pair $((\text{CH}_3)_3\text{NH}^+/\text{Br}^-)$, even in the gas phase [7].

Of these complexes, $\text{H}_3\text{N}-\text{HCl}$ is the most extensively studied, with experimental [8, 9] and theoretical [10-12] studies dating back several decades. The complex was first studied by infrared spectroscopy in 1973, when it was observed in a nitrogen matrix [13]. Later, differences between the spectra in nitrogen and argon matrices were noted [14], and in turn, the interaction in this system was described as a proton-shared hydrogen bond [3, 15]. However, results from gas-phase rotational spectroscopy were consistent with a complex that had a reasonably strong hydrogen bond, but very little proton transfer [7, 15]. The implication is that matrix media provide sufficient solvent stabilization to affect the extent of proton transfer in this complex. The broader extent of the matrix effects on $\text{H}_3\text{N}-\text{HCl}$ were not fully realized until its IR spectrum was recorded in solid neon as well as neon/argon mixtures [16, 17]. In the neon matrix, the H-Cl stretching frequency was much less than that observed in argon or nitrogen, and consistent with a strong hydrogen-bonded complex, just “slightly stronger than in the gas-phase complex.” [17] Taken together, these results indicate that these media cause a progressive strengthening of the hydrogen bond and/or a greater degree of proton transfer across the various host environments, in accord with their charge stabilizing ability ($\text{Ne} < \text{Ar} < \text{N}_2 < \text{Kr}$) [17].

Just prior to the neon matrix observations, Jordan and Del Bene completed a thorough computational study of anharmonicity and matrix effects in $\text{H}_3\text{N}-\text{HCl}$ using MP2/aug'-cc-pVDZ

calculations [18]. In total, four complexes were examined: $(\text{CH}_3)_3\text{N-HBr}$, $(\text{CH}_3)_3\text{N-HCl}$, $\text{H}_3\text{N-HBr}$, and $\text{H}_3\text{N-HCl}$, which had binding energies of -26.7, -17.8, -10.0, and -9.5 kcal/mol, respectively, and as-a-whole, these results are consistent with Legon's observations regarding the effects of amine and HX substituents [7]. Though this study employed a rather low-level of theory by current standards, the analysis was thorough and sophisticated; it involved a 2-D mapping (N-H vs. H-Cl) potential surfaces and an assessment of the vibrational amplitude of the H atom in both the ground and first-excited H-X stretching states. As such the results were directly comparable to the experimental observations. Matrix effects were modeled via an applied electric field, which manifested a distinct increase in the extent of proton transfer with increasing field strength, and this approach was reasonably effective in accounting for matrix frequency shifts. Previous studies [19], which employed an analogous approach to the potential but treated the matrix via explicit inclusion of noble gas atoms in the complex (e.g., $(\text{Ar})_3\text{-H}_3\text{N-HCl}$), failed to account for the observed shifts in the IR spectra.

In this paper, we report experimental IR frequencies for two isotopic forms of $\text{CH}_3\text{CN-HCl}$ in solid neon, as well as a modeling study of condensed-phase effects on structure and bonding for both $\text{CH}_3\text{CN-HCl}$ and $\text{H}_3\text{N-HCl}$. Our initial interest in $\text{CH}_3\text{CN-HCl}$ was somewhat serendipitous. During our recent study of the IR spectrum of $\text{CH}_3\text{CN-BCl}_3$ in solid neon [20], we experienced some difficulties with impurity HCl, and in order to distinguish between the lines for $\text{CH}_3\text{CN-HCl}$ and $\text{CH}_3\text{CN-BCl}_3$, we recorded IR spectra of CH_3CN and HCl in solid neon. While the gas-phase structure of $\text{CH}_3\text{CN-HCl}$ has been determined by rotational spectroscopy [21], and IR spectra of have been observed previously in nitrogen and argon matrices [22] and in even in silicalite (a zeolite) [23], reports of the spectrum in solid neon were limited to a few unpublished frequencies

for the primary isotopomer noted in reference 17. In due course, we noticed a trend in ν_{HCl} bands that was reminiscent of that noted above for $\text{H}_3\text{N-HCl}$, though the overall dynamic range of the spectral shifts was much less. Nonetheless, we were intrigued by the occurrence of this effect in a much weaker system, and set out to model the effects of the bulk, condensed phase environments on the structural properties of $\text{CH}_3\text{CN-HCl}$ using an approach based on that used in our studies of Lewis acid-base systems (*e.g.*, $\text{CH}_3\text{CN-BF}_3$)[24]. Previous studies of frequency shifts in $\text{CH}_3\text{CN-HCl}$ are limited to a semi-empirical study that addressed the effects of Xe and CCl_4 solutions using a rigorous, pseudo-triatomic molecule framework [25], and it achieved qualitative agreement with experiment. In the present case, we chose to extend the scope of our study to include $\text{H}_3\text{N-HCl}$, because the matrix effects are much more pronounced, and have been thoroughly characterized by both experiment and theory (*vide supra*). Overall, our analysis is arguably less sophisticated than that of Jordan and Del Bene [18], in that we employ a 1-D representation of the potential, and neglect to investigate the vibrational amplitude directly. However, our primary focus is the underlying chemical effects that drive changes in structure and bonding, and also, we sought an accessible protocol that could be readily adopted by other interested researchers who have access to modern computational methodologies. One advantage of the present study is that we are afforded more options in terms of electronic structure methods than in reference 18, including modern implementations of density functional theory, higher-levels of post-Hartree-Fock theory, and larger basis sets. Another key difference is that we represent the bulk, condensed-phase media with continuum solvation models [26], which we have used successfully in our past work [24], and in turn, makes the correspondence to the experimental sample conditions more straightforward. In the end, the model results are largely consistent with the implications of the observed spectral shifts, and also provide some underlying mechanistic insight into the changes in

structure and bonding that underlie matrix effects as well as the factors that manifest differences between CH₃CN–HCl and H₃N–HCl in terms of their medium sensitivity.

Methods

Materials

CH₃CN (g) was obtained from the ambient vapor pressure of the liquid by placing a few mL of liquid CH₃CN (VWR, >99.5%) in a 25 mL sample tube (Chemglass AF-0092) that was connected to a preparatory gas manifold (Chemglass AF-0300-03). The liquid sample was purified via several freeze-pump-thaw cycles immediately prior to gas mixture preparation. Gases, including both HCl (Matheson, Technical Grade) and neon (Praxair, >99.999%), were used without further purification. Gas mixtures, CH₃CN or HCl in neon, were prepared in 2-liter glass bulbs (Chemglass, AF-0093), and concentrations ranged from 1/400 to 1/1600 (HCl/Ne or CH₃CN/Ne). The preparatory manifold was maintained at a pressure of about 2×10^{-4} Torr using a glass diffusion pump (Chemglass AF-0330).

Low- Temperature Infrared Spectra

Matrix isolation-IR experiments were performed on an apparatus described previously [27, 28]. Matrix samples were prepared by flowing the CH₃CN/Ne and HCl/Ne mixtures through separate Teflon lines fitted with stainless steel compression fittings. Flows were controlled using Granville-Phillips #203 leak valves, and flow rates for each mixture varied from 4-10 mmol/hour. The separate HCl/Ne and CH₃CN/Ne gas streams were merged immediately prior to entering the cryostat chamber using a previously described concentric dual-deposition flange [27], and ultimately, the matrix sample was condensed on a gold-plated mirror. Sample temperature was controlled and maintained using a Lakeshore 331 temperature controller and two silicon diodes; one behind the sample window and

another near the end of the second refrigeration stage. Spectra were recorded using a Thermo Nicolet Nexus 670 FTIR at 1 or 2 cm^{-1} resolution, and typically 400 scans were averaged. In most instances, two to three depositions of 30-60 minutes each were performed with the sample mirror at 6K, and spectra were recorded after each one. Often, the sample was annealed to 9K for 60 minutes after the final deposition, and additional spectra were recorded. Optimum signals were obtained with relatively low HCl concentrations ($< 1/1600$); those displayed in the figures below were obtained with guest-host ratios of 1/2/3200 (HCl/CH₃CN/Ne).

Computations

All computations were performed using Gaussian 09 [29] versions B.01 and D.01. Equilibrium geometries were obtained within the C_{3v} point group, and all gas-phase optimizations were performed using the “opt=tight” option with an “ultrafine” integration grid, while standard convergence criteria were employed for optimizations in dielectric media. Seeking a prediction of the gas-phase H-Cl stretching frequency for CH₃CN-HCl, we initially attempted a validation study based on the prediction of the frequency of free HCl, akin to our previous studies of Lewis acid-base systems [30, 31]. In this process, we explored the performance of 18 different density functionals as well as MP2, and found that anharmonic frequency predictions were essential to obtain any reasonable agreement with the experimental frequency [32]. However, when we used the best of these methods (B3PW91, HSEh1PBE, *m*PW1PW91, and TPSSh) to predict the HCl stretching frequency for CH₃CN-HCl, the complex-induced frequency shift (*i.e.*, CH₃CN-HCl vs. free HCl) was overestimated; the predicted frequency was less than that measured in the neon matrix. We note that a similar effect is reflected in the predictions of the ν_{HCl} band for H₃N-HCl reported in reference 18. In that instance, the predictions based on an MP2/aug'-cc-pVDZ potential surface also lied below the experimental, neon-matrix value

(which was measured after the theoretic study was published) [17]. Lacking any reliable method for gas-phase frequency predictions, or any other clear validation criteria by which to select the optimum computational method for structure and frequency calculations, we opted to use M06, a density functional known to accurately reproduce H-bond energies [33], as well as two wave function-based methods, MP2 and CCSD. We do note that all three of these methods yield favorable agreement with the experimental structure of CH₃CN–HCl [21]. However, the M06 frequency prediction does not seem reliable, even after applying a scale factor (*vide infra*). The aug-cc-pVTZ basis set was used exclusively throughout this work [34].

We also mapped N–Cl potential energy curves for both CH₃CN–HCl and H₃N–HCl. These curves were constructed in a point-wise manner, at a series of fixed distances ranging from 2.3 to 4.5 Å, in 0.1 Å steps. Subsequently, a few intermediate points were added near the minima to make the plotted curves appear more continuous. Additionally, to explore the effects of the condensed-phase environments on these potentials, we obtained hybrid N–Cl potential curves, comprised of the sum of gas-phase electronic energy (M06/aug-cc-pVTZ) and the electrostatic component of the solvation free energy (PCM/M06/aug-cc-pVTZ)[26] at a series of dielectric constants (1.2, 1.5, 2.0, 3.0, 5.0, and 10.0) for each point on the potential [24]. For various points on the N–Cl curves, we obtained atomic charges via Natural Population Analyses (NPA) [35], which was executed directly in Gaussian. In addition, we also computed a few scans of the H–Cl potential for CH₃CN–HCl, which ranged from 1.1 to 2.0 Å in 0.1 Å increments, with the CH₃CN subunit held at a series fixed distances of from 1.6 to 2.4 Å (0.2 Å increments) from the H atom. For the R(N–H) = 2.2 Å curve, we also obtained the hybrid potential in a dielectric medium (ϵ = 2.0).

Results and Discussion

Infrared Spectra

Infrared spectra of matrices containing CH₃CN and/or HCl in solid neon are displayed in Figure 1 (the C-N stretching (ν_{CN}) region: 2200-2400 cm⁻¹) and Figure 2 (the H-Cl stretching (ν_{HCl}) region: 2600-3000 cm⁻¹). In these spectra, we observed product bands, *i.e.*, peaks that require the presence of both CH₃CN and HCl, at: 2756, 2677, 2589/2570, 2308, 2279, 2275 (broad), 926, 800, 739, and 719 cm⁻¹. The peaks at 2308, 2279, 926, 739, and 719 cm⁻¹ are consistent with those observed by Schriver *et al.* for CH₃CN-HCl in argon (2267, 918.2, 728, and 720 cm⁻¹) and/or nitrogen matrices (2309, 2278, 930 cm⁻¹)[22]. Furthermore, a subset of these peaks: 2308, 2279, 926, and 739 cm⁻¹; grow slightly upon annealing and exhibit a consistent set of relative intensities across all conditions. As such, we tentatively assign these peaks to the 1:1 CH₃CN-HCl complex. Specific mode assignments for these peaks will be discussed in detail immediately below.

Figure 1. Neon-matrix spectra of the 2200-2400 cm⁻¹ region. The guest-host ratio for this sample is 1/2/3200 (HCl/CH₃CN/Ne). * indicates CH₃CN-HCl peaks.

Figure 2. Neon-matrix spectra of the 2600-3000 cm⁻¹ region. The guest-host ratio for this sample is 1/2/3200 (HCl/CH₃CN/Ne). * indicates CH₃CN-HCl peaks.

The remaining product band at 2677 cm^{-1} , by far the most intense of the set, lies in the region expected for the H-Cl stretch (ν_{HCl}) but is not entirely consistent with the frequencies reported by Schriver et al. (Ar: 2662 cm^{-1} ; N₂: 2576 cm^{-1})[22], and furthermore it also differs from the H-Cl stretching frequency observed for gas-phase CH₃CN-HCl (a broad feature centered at 2725 cm^{-1}) [36]. Nonetheless, because this peak exhibits consistent relative intensities with the other product bands assigned to CH₃CN-HCl, we assigned this to the H-Cl stretching frequency in the 1:1 complex. This assignment is consistent with the result reported in reference 17, though no rationale is provided for that assignment. In turn, we presume the broader feature at 2589 cm^{-1} , which appears only at relatively high guest concentrations, is due to a larger cluster involving CH₃CN and HCl. We note that the range of values for the H-Cl stretching frequency is significant ($\sim 160 \text{ cm}^{-1}$), and that the shifts are systematic and parallels the charge-stabilizing ability of the matrix medium (Ne < Ar < N₂) [22]. This seems to indicate that the subtle environmental changes across these media affect the strength of the hydrogen bond in the complex.

In IR spectra of neon matrices containing CD₃CN and HCl, product bands were observed at: 2756, 2677, 2589/2570, 2293, 2284, 838, 772, 736, and 683 cm^{-1} . Of these, the peaks at 2677, 2293, and 838 cm^{-1} have consistent relative intensities across all conditions and grow upon annealing, in indication they arise from CD₃CN-HCl. The 2677 cm^{-1} peak is entirely consistent with the ν_{HCl} band for the primary isotopomer, thus adding some credibility to the peak assignment noted above. In the ν_{CN} region (about 2250-2300 cm^{-1}), we observed two bands for the primary isotopomer (2308/2279 cm^{-1}), presumably due to the Fermi resonance in CH₃CN [37], which seems to persist upon coordination with HCl. In CD₃CN, the Fermi resonance is apparently disrupted, and in the CD₃CN/HCl spectra, only a single product band is observed in this region, a doublet centered near 2290 cm^{-1} . Initially, we had

thought that the pair of bands at 2293 and 2284 cm^{-1} was a doublet arising from distinct trapping sites in the matrix, but the 2284 cm^{-1} counterpart exhibits inconsistent intensity ratios, and is more sensitive to annealing than the 2293 cm^{-1} peak. Since these consistent product bands for each isotopomer are shifted only 10-20 cm^{-1} to the blue of the corresponding ν_{CN} bands for free CH_3CN or CD_3CN , and for the CD_3CN -containing complex, the computational prediction is within 10 cm^{-1} of the observed peak, we confidently assign the peaks in this 2250-2300 cm^{-1} region to the ν_{CN} bands in the 1:1 complexes: 2308/2279 cm^{-1} for $\text{CH}_3\text{CN-HCl}$; 2293 cm^{-1} for $\text{CD}_3\text{CN-HCl}$.

As for the remaining product bands, we turn first to those observed at 926 cm^{-1} for $\text{CH}_3\text{CN-HCl}$, and 838 cm^{-1} for $\text{CD}_3\text{CN-HCl}$. These bands lie in the region of the C-C stretching band (ν_{CC}), which occurs at 920 cm^{-1} for CH_3CN and 831 cm^{-1} for CD_3CN [38]. Thus, the D-3 isotope shift for the free nitrile is -89 cm^{-1} , and the observed difference in the product bands is ($\text{CH}_3\text{CN/HCl} - \text{CD}_3\text{CN/HCl}$) is 88 cm^{-1} , and thus we assign these bands to the ν_{CC} modes in the complexes: 926 cm^{-1} for $\text{CH}_3\text{CN-HCl}$, and 838 cm^{-1} for $\text{CD}_3\text{CN-HCl}$. We note that the isotope shift predicted by M06/aug-cc-pVTZ calculations is slightly larger, about 100 cm^{-1} . Finally, we note that we lack clear mode assignments for the remaining product bands in the 700-800 cm^{-1} region (739 cm^{-1} for $\text{CH}_3\text{CN/HCl}$; 772 and 736 cm^{-1} for $\text{CD}_3\text{CN-HCl}$). These do exhibit relative intensities that are largely consistent with those peaks mentioned above, but the absence of fundamental bands in this region, either those corresponding to motions within complex subunits or those predicted for the complexes, complicates a definitive mode assignment. Table 1 summarizes mode assignments for the assigned product bands, and M06/aug-cc-pVTZ predictions (*vide infra*) are listed there as well.

Table 1. Measured and calculated frequencies^a

	CH ₃ CN–HCl		CD ₃ CN–HCl	
	Experimental	Computational ^b	Experimental	Computational ^b
ν_{HCl}	2677	2675	2677	2675
ν_{CN}	2308/2279	2284	2293	2284
ν_{CC}	926	953	838	847

a) Units of cm^{-1} . b) Computational frequencies via M06/aug-cc-pVTZ. Values for the C-N stretching band were scaled by a factor of 0.9525, determined in ref. 20. Values for the H-Cl stretching band were scaled by a factor of 0.978, determined from the ratio of the gas-phase band center to calculated (M06) frequencies (see text for discussion).

Equilibrium Structures, Binding Energies, and Calculated Frequencies

To better understand the nature of the matrix-induced spectral shifts, we undertook a computational study of CH₃CN–HCl, and also, we examined H₃N–HCl; a system for which these effects are extreme and have been thoroughly investigated via computations (*vide supra*). Minimum energy structures and binding energies of gas-phase CH₃CN–HCl and H₃N–HCl were obtained via M06, MP2, and CCSD calculations and the aug-cc-pVTZ basis set. The N–H distance of CH₃CN–HCl was found to be 1.967 Å, 1.946 Å, and 2.037 Å via M06, MP2, and CCSD, respectively, and the corresponding H-Cl distances were 1.302 Å, 1.292 Å, and 1.288 Å. For reference, the H-Cl distance in free HCl (M06) is 1.283 Å, indicating that the H-Cl bond lengthens by about 0.02 Å in the complex. The experimental N–Cl distance, which is the primary result from the gas-phase structure analysis, is 3.301 Å [21], and all of the theoretical results agree to within 0.05 Å (3.269 Å for M06, 3.238 Å for MP2, and 3.325 Å for CCSD). The binding energies calculated for CH₃CN–HCl via M06, MP2, and CCSD were 6.0, 6.7, and 6.0 kcal/mol, respectively. The consistency among the binding energies from these three distinct computational methods is noteworthy, and furthermore, the M06 structure parameters lie between the MP2 and CCSD values. We also note that M06 out-performs two older hybrid density functionals

tested in the validation study noted above that have provided reliable structure results on nitrile-BF₃ complexes in our previous work [30, 31] (B3PW91 and *m*PW1PW91). The calculated N--Cl distances from these methods are 3.244 Å and 3.233 Å, respectively. A complete set of structure parameters is displayed in Figure 3, and we note that we chose to highlight the M06 results for reasons noted above, and to display results from a method consistent with the analysis of the potential; but the CCSD results are also included to facilitate a comparison with a wave function-based theory.

Figure 3. Gas-phase structure of CH₃CN-HCl via M06/aug-cc-pVTZ, with CCSD/aug-cc-pVTZ data included in parentheses. The binding energy via either method is 6.0 kcal/mol.

For H₃N-HCl, the N--H, hydrogen bond distances were 1.814 Å, 1.738 Å, and 1.851 Å for M06, MP2, and CCSD, respectively, and the corresponding H-Cl bond lengths were 1.328 Å, 1.328 Å, and 1.311 Å (Figure 4). The experimental N-Cl distances for this complex is 3.136 Å [7], and the corresponding M06, MP2 and CCSD results are 3.142 Å, 3.066 Å, and 3.162 Å, respectively. As a whole, the computational results are less consistent than those for CH₃CN-HCl, but the M06 and CCSD results agree quite well with experiment. Also, for H₃N-HCl, the elongation of the H-Cl bond is more significant (0.045 Å via M06). Both the shorter N--H distance and the more elongated H-Cl bond are consistent with a stronger hydrogen bond than in CH₃CN-HCl, and the calculated binding energies

confirm this, and were found to be 8.6, 9.2, and 7.7 kcal/mol via M06, MP2, and CCSD, respectively. The predicted binding energies among the three methods are somewhat less consistent for this system, but again the M06 results are intermediate relative to MP2 and CCSD, for both structure and energy in this case. Regardless, the larger binding energies are consistent with the difference in base strength; the proton affinity values for CH₃CN and NH₃ are 186 and 204 kcal/mol, respectively [38]. In reference 3, Ault *et al.* define a normalized proton affinity difference (Δ) defined by equation (1) below for a B--H-A complex, *viz.*

$$\Delta = \text{PA(B)} - \text{PA(A}^-) / \text{PA(B)} - \text{PA(A}^-) \quad (1)$$

This parameter is usually negative, and decreases in magnitude as the extent of proton transfer increases. For example, it is -0.343 for H₂O–HCl, a Type 1, hydrogen-bonded complex, and -0.175 for (CH₃)₃N–HBr a Type 3 proton transfer complex [3]. The value for H₃N–HCl is -0.24, near that deemed optimal for a Type II, proton-shared complex; and thus consistent with IR spectra in argon and nitrogen matrices (though as noted above, this results from a slight solvent stabilization). For CH₃CN–HCl, Δ = -0.28, which is larger in magnitude than Δ for H₃N–HCl, essentially coincident with the value for (CH₃)₂O–HCl [3], and consistent with a relatively strong Type I complex, which presumably be would be less apt to transition to a Type II complex with marginal degree of solvent stabilization. Thus, the computational results for the structural and energetic properties of these systems are consistent with empirical estimates based on gas-phase basicity data.

Figure 4. Gas-phase structure of $\text{H}_3\text{N-HCl}$ via M06/aug-cc-pVTZ, with CCSD/aug-cc-pVTZ data included in parentheses. The M06/aug-cc-pVTZ and CCSD/aug-cc-pVTZ binding energies are 8.6, and 7.7 kcal/mol, respectively.

Calculated frequencies (M06/aug-cc-pVTZ) for the measured bands of $\text{CH}_3\text{CN-HCl}$ are listed in Table 1 with the experimental data. In an attempt to improve the accuracy of the predictions for the C-N (ν_{CN}) and the H-Cl (ν_{HCl}) stretching frequencies, a scaling procedure was applied. We have noted poor agreement between experiment and theory for ν_{CN} frequencies in our previous work [20, 39]. As such, for the ν_{CN} mode, we applied a factor of 0.9525, previously determined from the ratio of the observed to calculated ν_{CN} frequencies for CD_3CN [20], and as a result the calculated frequency was within 10 cm^{-1} of the experimental frequency. In addition, we noted above that computational predictions overestimate the red-shift of the ν_{HCl} band in $\text{CH}_3\text{CN-HCl}$. For this mode, we obtained a scale factor of 0.978 from a ratio of frequencies for un-complexed HCl; the experimental ν_{HCl} band center [32] divided by the predicted, harmonic M06/aug-cc-pVTZ value. We find that the scaled M06 value (2675 cm^{-1}) agrees poorly with the experimental gas-phase result (2725 cm^{-1}), though we also note that the measured value was estimated from a broad absorption band which ranges from $2700\text{--}2800\text{ cm}^{-1}$ [36]. Furthermore, the scaled-M06 value lies just a few cm^{-1} lower than the measured neon-matrix value, which does not seem reasonable and thus further undermines any confidence in the M06 prediction. Regardless, a comparison between the experimental gas-phase and solid neon values suggests a matrix shift of about 50 cm^{-1} .

The analogous, scaled-M06 prediction for the gas-phase ν_{HCl} frequency for $\text{H}_3\text{N}-\text{HCl}$ yields a value of 2300 cm^{-1} , roughly 220 cm^{-1} above the observed neon matrix value (2084 cm^{-1}) [17]. The prediction is quite consistent with the harmonic, MP2/aug'-cc-pVTZ values in reference 18 (2289 cm^{-1} based on the full potential surface, 2278 cm^{-1} based on a pseudo-triatomic surface) [18], but we note again that the anharmonic predictions (1905 cm^{-1} from a 1-D surface, and 1567 cm^{-1} from a 2-D surface) [18] depict a shift that exceeds the measured neon-matrix value. Thus it appears that, much like our experience noted above predicting ν_{HCl} for $\text{CH}_3\text{CN}-\text{HCl}$, the extent of anharmonicity is overestimated, an indication that the computational methods do not accurately model the potential at large displacements. In any event, Andrews previously suggested that the IR spectrum in neon implied a complex with a slightly stronger hydrogen bond than in the gas phase, and reliability notwithstanding, M06 prediction appears to be marginally consistent with that assessment.

Frequency Shifts and Medium Effects on Equilibrium Structure

The overall shifts of the ν_{HCl} band across various media for $\text{CH}_3\text{CN}-\text{HCl}$ are shown schematically in Figure 5, and include not only data from previous matrix IR studies [22], but also data from the gas-phase [36], liquid xenon and CCl_4 [25], and in a silicalite-based zeolite [23]. To a great extent, the shift of the ν_{HCl} band tends to parallel the charge stabilizing ability of the medium; the exception may be the nitrogen matrix data. To further illustrate this trend and cast it in terms of an established physical quantity, we plotted the medium-induced frequency shifts (medium – gas, measured) vs. polarizability [40]. This plot is displayed in Figure 6 (*left*), and with the exception of the nitrogen-matrix data [22], the frequency shifts tend to follow a continuous curve. It is not clear as to why the nitrogen-matrix frequency is an outlier, but it may reflect that N_2 is the only one of these substances

with a non-zero quadrupole moment, and thus it may offer some additional electrostatic stabilization that is lacking in the other hosts. In any event, the data indicate that the medium causes a systematic strengthening of the hydrogen bond between CH_3CN and HCl , and moreover, that the ability of the medium to stabilize charge is a key underlying factor. The overall trend in these frequency shifts resembles that observed for $\text{H}_3\text{N}-\text{HCl}$ [17], but the dynamic range is much less; the frequencies span about 160 cm^{-1} in the case of $\text{CH}_3\text{CN}-\text{HCl}$, and over 1500 cm^{-1} in the case of $\text{H}_3\text{N}-\text{HCl}$, though the latter situation is complicated by coupling between the ν_{HCl} and other symmetric modes as proton transfer progresses [14]. We also constructed a similar plot frequency shift vs. polarizability for $\text{H}_3\text{N}-\text{HCl}$ (Figure 6, right). Even with the greater dynamic range, the points, again with the exception of the nitrogen data, tend to follow a continuous curve, though there are fewer data than for $\text{CH}_3\text{CN}-\text{HCl}$.

Figure 5. Schematic of ν_{HCl} frequency shifts for $\text{CH}_3\text{CN}-\text{HCl}$ across various media. The (scaled) M06 and Ne data are from this work. The Ar and N_2 frequencies are from ref. 22, the gas-phase data are from ref. 36, the Xe and CCl_4 data are from ref. 25, the zeolite data are from ref. 23.

Figure 6. Medium-induced frequency shifts of the ν_{HCl} bands in CH₃CN-HCl (left) and H₃N-HCl (right) vs. host/solvent polarizability. The CH₃CN-HCl data points reflect the difference between the measured matrix/solvent and gas-phase frequencies (medium-gas). The H₃N-HCl data points reflect the difference between the measured matrix and predicted (scaled M06) gas-phase frequencies (medium-gas/M06).

In an effort to obtain some rationale for the observed spectral shifts, and make a more direct connection to structural changes that accompany them, we examined the effect of dielectric media on the M06/aug-cc-pVTZ structures of these complexes using the PCM method [26] for a range of dielectric constants (1.2, 1.5, 2.0, 5.0, and 10.0). The key structure parameters, at least in terms of conveying the effect of the medium on the strength hydrogen bond interaction are the N-H and H-Cl distances, and these are listed in Tables 2 and 3 for CH₃CN-HCl and H₃N-HCl, respectively. The data for CH₃CN-HCl do reveal a slight contraction of the N-H hydrogen bond, by about 0.1 Å in total by $\epsilon=10$, and the corresponding effect on the H-Cl bond is a lengthening of about 0.01 Å. The trend is systematic and progressive, however, and is discernable even in the low-dielectric values typical of noble gas matrices (1.2 and 1.5) [27]. The effect on H₃N-HCl is analogous, though much more

dramatic, as the N-H distance lengthens by over 0.7 Å by $\epsilon=10.0$, and the H-Cl distance elongates by over 0.6 Å. The H₃N-HCl data also convey more extreme effects at the low dielectric values. As a whole, the data in both Tables are consistent with observations; a rather subtle matrix effect for CH₃CN-HCl, and a more substantial matrix effect for H₃N-HCl.

Table 2. N-H and H-Cl Distances for CH₃CN-HCl in Bulk Dielectric Media^a

Dielectric constant	N-H distance (Å)	H-Cl distance (Å)
1.0 (gas)	1.966	1.302
1.2	1.950	1.304
1.5	1.933	1.306
2.0	1.912	1.308
3.0	1.889	1.310
5.0	1.869	1.313
10.0	1.852	1.315

a) Results from PCM/M06/aug-cc-pVTZ, with standard convergence limits.

Table 3: N-H and H-Cl Distances for H₃N-HCl in Bulk Dielectric Media^a

Dielectric constant	N-H distance (Å)	H-Cl distance (Å)
1.0 (gas)	1.814	1.328
1.2	1.777	1.335
1.5	1.719	1.348
2.0	1.273	1.570
3.0	1.110	1.810
5.0	1.083	1.889
10.0	1.070	1.945

a) Results from PCM/M06/aug-cc-pVTZ, with standard convergence limits.

Potential Curves

To gain a broader insight into the effects of dielectric media on the intermolecular potential of these complexes, we examined the N-Cl potential curves for CH₃CN-HCl and H₃N-HCl, both in the gas phase and in bulk dielectric media. The gas-phase curves are displayed in Figures 7 and 8 for CH₃CN-HCl and H₃N-HCl, respectively, and they consist of the gas-phase electronic energy (M06, MP2, and CCSD, with aug-cc-pVTZ), plotted relative to the energies of the corresponding fragments. The three methods provide very consistent results for these potentials, especially for the CH₃CN complex, and again, the M06 results are intermediate between those from MP2 and CCSD. For CH₃CN-HCl, the minimum energy point occurs at $R(\text{N-Cl}) = 3.3 \text{ \AA}$ on the M06 and CCSD curves, and at $3.2 \text{ \AA}$ on MP2 curve, with energy values of -6.0, -6.0, and -6.7 kcal/mol, respectively (equivalent to the binding energies quoted above). For H₃N-HCl, and the minimum energy points for M06 and MP2 methods occur at $3.1 \text{ \AA}$ with values of -8.6 and -9.2 kcal/mol; for CCSD, the minimum energy point is at $3.2 \text{ \AA}$ at a value of -7.7 kcal/mol (again equivalent to the quoted binding energies above). The stronger hydrogen bonding interaction in H₃N-HCl is illustrated by the depth of its potential energy curve, and that the minimum occurs at a shorter distance. Furthermore, we note that the inner wall of the potential is steeper in CH₃CN-HCl; which indicates that more energy would be required to progress along this curve toward shorter N-H distances and/or the eventual transfer of the proton from Cl to N. This is feature reflected by the longer distance at which the curves exceed the vertical scale in Figure 7. For a quantitative assessment, we note that the (M06) energy of the CH₃CN complex at $R(\text{N-Cl}) = 2.8 \text{ \AA}$ is -0.1 kcal/mol, while the energy for the NH₃ complex at this point is -6.5 kcal/mol. Relative to the respective minima, however, the H₃N-HCl potential rises somewhat more quickly, in part because the minimum lies at lower energy than that for CH₃CN-HCl.

Figure 7. N-Cl Potential energy curves for $\text{CH}_3\text{CN-HCl}$ via M06, MP2, and CCSD and the aug-cc-pVTZ basis set.

Figure 8. N-Cl Potential energy curves for $\text{H}_3\text{N-HCl}$ via M06, MP2, and CCSD and the aug-cc-pVTZ basis set.

We assessed the extent of proton transfer at various points along these curves by examining changes in the H-Cl and N-H distances, as well as atomic charges from a Natural Population Analysis (NPA) [35]. We did identify some shifts in these quantities along the inner wall of the curves, but the effects are subtle for the most part, at least on the gas-phase curves (*vide infra*). For $\text{CH}_3\text{CN-HCl}$, the H-Cl distance remains at about $1.3 \text{ \AA}$ throughout most of the curve (ranging from $1.300 \text{ \AA}$ at $R(\text{N-Cl}) = 3.5 \text{ \AA}$ to $1.307 \text{ \AA}$ at $R(\text{N-Cl}) = 2.8 \text{ \AA}$), but does elongate by about $0.02 \text{ \AA}$ near the inner limit of the potential scan. The HCl distance at $R(\text{N-Cl}) = 2.6 \text{ \AA}$ is $1.322 \text{ \AA}$, where the N-H distance is $1.278 \text{ \AA}$, still significantly longer than a typical N-H covalent bond (*e.g.*, about $1.0 \text{ \AA}$ in Figure 4), in spite of the fact that the HCl moiety has been constrained at short range. The NPA charge on the chlorine atom near the equilibrium geometry ($R(\text{N-Cl}) = 3.3 \text{ \AA}$) is -0.33 (units of elementary charge). Also, there is a steady shift in the NPA charges along the curve, but the charge on the Cl ranges only from -0.31 to -0.39 between $R(\text{N-Cl}) = 3.5$ and $2.8 \text{ \AA}$, respectively. A more sudden shift, to -0.46 , occurs by $2.6 \text{ \AA}$; in the

region of the H-Cl bond elongation. Nonetheless, this indicates only a marginal shift towards an ionic structure, even along the inner wall of the potential where we have constrained the N-Cl distance to sub-optimal values.

An analogous examination of the points along the $\text{H}_3\text{N-HCl}$ curve indicates a somewhat more significant effect on structure and bonding along the inner potential wall. In this case, the elongation of the H-Cl bond sets in at a slightly longer N-Cl distance, and the H-Cl bond elongates by about 0.1 Å; the H-Cl distance at $R(\text{N-Cl}) = 2.8$ Å is 1.44 Å, longer than the N-H distance at that point on the curve (1.360 Å). In addition, the NPA charges reflect a greater tendency for proton transfer. Near the equilibrium geometry ($R(\text{N-Cl})=3.3$ Å), the NPA charge on the chlorine atom is -0.38; 0.05e more negative than in the case of $\text{CH}_3\text{CN-HCl}$. The overall shift in the NPA charges with decreasing N-Cl distance is also more significant. Between $R(\text{N-Cl}) = 3.5$ Å and $R(\text{N-Cl}) = 2.8$ Å, the NPA charge on Cl ranges from -0.33 to -0.52, and then shifts to a value of -0.57 at $R(\text{B-Cl}) = 2.6$ Å. This suggests more of a shift toward an ion-pair-type structure when the HCl moiety is constrained at short range than in the case of $\text{CH}_3\text{CN-HCl}$, but perhaps short of what might be expected for a primarily ionic complex.

Figures 9 and 10 display the effects of bulk, dielectric media on the N-Cl potentials for $\text{CH}_3\text{CN-HCl}$ and $\text{H}_3\text{N-HCl}$, respectively. These curves were constructed by adding the electrostatic component of the solvation free energy (via PCM/M06/aug-cc-pVTZ) with the minimum energy plotted relative to the sum of the CH_3CN and HCl gas-phase electronic energies. For $\text{CH}_3\text{CN-HCl}$, the overall changes only slightly increasing dielectric constant (ϵ). The minimum energy point on the gas-phase curve lies at 3.3 Å, but this shifts to 3.2 Å for a dielectric constant of 1.5 or above. There is also a subtle reduction in the steepness of the inner wall with increasing dielectric. The energy rise at 2.8 Å, relative to the value

at 3.3 Å is +5.9 kcal/mol in the gas phase, but decreases to +5.5 and +5.1 kcal/mol for ϵ values of 1.2 and 1.5, respectively. This is consistent with a subtle enhancement of the hydrogen bonding interaction in low dielectric media (ϵ is about 1.2 for solid neon, and 1.4-1.5 for solid argon and nitrogen, see reference 24 for discussion). The trend persists at higher dielectrics as well; ΔE (again at 2.8 Å relative to 3.3 Å) is reduced to +4.2 kcal/mol for $\epsilon = 3$, and +3.5 kcal/mol for $\epsilon = 10.0$. This effect on the potential is accompanied by a marginal increase in the HCl distance and a concurrent decrease in the N-H distance. Again at 2.8 Å, the gas-phase HCl distance is 1.307 Å, and a slight, steady increase is noted as the dielectric constant is increased; $R(\text{H-Cl})$ is 1.320 Å at $\epsilon = 1.5$, 1.341 Å at $\epsilon = 3.0$, and 1.378 Å at $\epsilon = 10.0$. The corresponding N-H distances are 1.480 Å, 1.459 Å, and 1.422 Å, and indicate a concurrent increase in the bonding between the N and H atoms. The negative charge on the Cl atom also increases with dielectric along in the inner region of the curve. The charge on Cl at $R(\text{N-Cl}) = 2.8$ Å is -0.39 in the gas phase, and the negative charge increases to -0.41 at $\epsilon = 1.5$, -0.44 at $\epsilon = 3.0$, and -0.48 at $\epsilon = 10.0$. Thus, these analyses indicate that as the medium enhances the hydrogen bond, the bonding does shift marginally in the direction of increased proton transfer from Cl to N, but the overall extent of this effect is slight. This is, in a general sense, consistent with the relatively

Figure 9: N-Cl potentials for $\text{CH}_3\text{CN-HCl}$ in the gas-phase ($\epsilon=1$; M06/aug-cc-pVTZ) and in bulk dielectric media (PCM/aug-cc/pVTZ) with dielectric constants (ϵ) varying from 1.5 to 10.

Figure 10: N-Cl potentials for $\text{H}_3\text{N-HCl}$ in the gas-phase ($\epsilon=1$; M06/aug-cc-pVTZ) and in bulk dielectric media (PCM/aug-cc/pVTZ) with dielectric constants (ϵ) varying from 1.5 to 10.

By contrast, the shape of the $\text{H}_3\text{N-HCl}$ potential changes dramatically with ϵ value. Most notably, minimum energy point shifts from $R(\text{N-Cl}) = 3.1 \text{ \AA}$ in the gas phase, to $R(\text{N-Cl}) = 2.8 \text{ \AA}$ for a dielectric constant of 2.0 or greater. Moreover, the curves for low-dielectric media ($\epsilon = 1.2$ and 1.5) are notably flat across a range spanning from 2.8 to 3.3 $\text{\AA}$, and the $\epsilon = 1.2$ curve exhibits two distinct minima, coincident with those for the gas-phase (3.1 $\text{\AA}$) and the higher dielectric constant curves (2.8 $\text{\AA}$). These peculiar, flat potentials are consistent with substantial enhancement of the hydrogen bonding interaction and partial proton transfer noted in argon and nitrogen matrices [14, 17] ($\epsilon = 1.4$ to 1.5 [24]). Charges and bond lengths at these points on the curve provide insight into the differences between the bonding at these key points on the curve (2.8 and 3.1 $\text{\AA}$). At $R(\text{N-Cl}) = 3.1 \text{ \AA}$ in the gas-phase curve, near the minimum energy structure (Figure 4), the H-Cl and N-H bonds are 1.332 and 1.768 $\text{\AA}$, respectively, while the Cl charge is -0.38. At $R(\text{N-Cl}) = 2.8 \text{ \AA}$ (still in the gas phase), near the high-dielectric minimum (Table 3), the H-Cl and N-H bonds are 1.440 and 1.360 $\text{\AA}$, respectively, while the Cl charge is -0.52 (as noted above). In dielectric media, there are significant, concurrent changes in the H-Cl and N-H distances, and in turn, a marked increase in the negative charge on Cl. First we examine the data for low-dielectric media, again at $R(\text{N-Cl}) = 2.8 \text{ \AA}$. The H-Cl distances at $\epsilon = 1.2$ and 1.5 are 1.468 and 1.502 $\text{\AA}$ respectively, while the corresponding N-H distances are 1.332 and 1.298 $\text{\AA}$, and the Cl charges are -0.55 and 0.59, respectively. These data indicate that even low dielectric media promote proton transfer to some extent in this complex, and this is qualitatively consistent with the assessment of the ionic character of the bonding in argon and nitrogen matrices, which has been estimated to be 40-50% based on correlations of the spectral shifts [15]. At the higher dielectric values, for which the $R(\text{N-Cl}) = 2.8 \text{ \AA}$ point is near the global minimum, the analogous data indicate a marked increase in proton transfer. As the dielectric is increase from 2.0 to 10.0, there is a steady

increase in the H-Cl bond distance (from 1.552 to 1.717 Å), a concomitant decrease in the N-H distance (from 1.248 to 1.083 Å), and the negative charge on Cl increases from -0.64 to -0.81. This N-H distance is only about 0.07 Å longer than that in Figure 4, which is representative of an N-H single bond. These data are consistent with a significant degree of proton transfer at higher dielectrics, which presumably reflects the ability of the media to stabilize the charge separation that accompanies the transition to an ionic structure. Nonetheless, this effect does not impact CH₃CN-HCl to the extent that it does H₃N-HCl; there is less proton transfer in the medium, and the energies remain higher along the inner potential wall, even with a great deal less ionic character in the bonding.

Finally, we did undertake a cursory examination of the H-Cl potential in CH₃CN-HCl, in an attempt to determine whether the dielectric media manifested any additional softening of the H-Cl bond beyond that induced by a contraction of the N-H hydrogen bond. To this end, we computed a series of H-Cl potential scans in the gas-phase (M06/aug-cc-pVTZ) for a series of fixed N-H distances (1.4, 1.6, 1.8, 2.0, and 2.2 Å). Not surprisingly, we observe a distinct softening of the potential that sets in between $R(\text{N-H}) = 2.0$ and 1.8 Å. This corresponds to $R(\text{N-Cl})$ distances of about 3.3 to 3.1 Å, which is just inside the minima on the N-Cl curves above. We also scanned the $R(\text{N-H}) = 2.0$ curve in a dielectric medium with $\epsilon = 2.0$, and we observed no significant, additional softening of the potential relative to the gas-phase. Thus, these results imply that the dielectric medium does not produce any direct effect on the H-Cl potential in-and-of-itself. Rather, the upshot seems to be that the medium acts to induce a slight enhancement of the hydrogen bond, which, upon a slight contraction of the N-H distance, leads to a softer H-Cl potential and ultimately, the frequency shifts.

Conclusions

We have observed and assigned several IR bands for two isotopic forms of the $\text{CH}_3\text{CN-HCl}$ complex in solid neon matrices at 6 K. While most of these bands appear at frequencies near those reported previously in argon and neon matrices [22], we ultimately noted that the ν_{HCl} band exhibited shifts that paralleled the charge-stabilizing ability of the inert, matrix media. In plots of these medium-induced frequency shifts versus polarizability of the host or solvent, points for both $\text{CH}_3\text{CN-HCl}$ and $\text{H}_3\text{N-HCl}$ revealed nearly-continuous trends; the exception in both cases was the data for nitrogen matrices. To better understand the underlying reasons for these shifts, as well as those in other media [23, 25], we undertook a computational study, and also extended it to the $\text{H}_3\text{N-HCl}$ complex. Equilibrium structural results are consistent with a stronger hydrogen bond in the ammonia complex, and moreover, that $\text{H}_3\text{N-HCl}$ undergoes major structural changes in dielectric media, consistent with significant proton transfer from Cl to N. On the other hand, the equilibrium structure of $\text{CH}_3\text{CN-HCl}$ changes only slightly in response to the dielectric media. We also explored the N-Cl potentials of the complexes, in the gas-phase and in dielectric media. For $\text{CH}_3\text{CN-HCl}$, the condensed-phase effects on the potential are rather subtle, but as-a-whole, the modeling results are consistent with a slight enhancement of the hydrogen bond in bulk condensed-phase environments, and in turn, subtle medium-induced shifts of the ν_{HCl} band. For $\text{H}_3\text{N-HCl}$, the predicted effects on the N-Cl potential are much more extreme, and also quite consistent with the extreme shifts observed for the ν_{HCl} band across various matrix media [17]. Charge analyses at various points along the curves are reasonably consistent with empirical estimates of the extent of proton transfer in low-dielectric environments [15], and furthermore, they illustrate differences in the bonding between $\text{CH}_3\text{CN-HCl}$ and $\text{H}_3\text{N-HCl}$ that accompany their distinct responses to condensed-phase media.

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