Interactions between the chloride anion and aromatic molecules: infrared spectra of the Cl-\_C6H5CH3, Cl-\_C6H5NH2 and Cl-\_C6H5OH complexes

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Interactions between the chloride anion and aromatic molecules: infrared spectra of the Cl\textsubscript{−}_C6H5CH\textsubscript{3}, Cl\textsubscript{−}_C6H5NH\textsubscript{2} and Cl\textsubscript{−}_C6H5OH complexes

Abstract
The Cl\textsuperscript{−}C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}:Ar, Cl\textsuperscript{−}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}:Ar, and Cl\textsuperscript{−}C\textsubscript{6}H\textsubscript{5}OH:Ar anion complexes are investigated using infrared photodissociation spectroscopy and ab initio calculations at the MP2/aug-cc-pVDZ level. The results indicate that for Cl\textsuperscript{−}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} and Cl\textsuperscript{−}C\textsubscript{6}H\textsubscript{5}OH, the Cl\textsuperscript{−} anion is attached to the substituent group by a single near-linear hydrogen bond. For Cl\textsuperscript{−}C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}, the Cl\textsuperscript{−} is attached to an ortho-hydrogen atom on the aromatic ring and to a hydrogen atom on the methyl group by a weaker hydrogen bond. The principal spectroscopic consequence of the hydrogen-bonding interaction in the three complexes is a red-shift and intensity increase for the CH, NH, and OH stretching modes. Complexities in the infrared spectra in the region of the hydrogen-bonded XH stretch band are associated with Fermi resonances between the hydrogen-stretching vibrational modes and bending overtone and combination levels. There are notable correlations between the vibrational red-shift, the elongation of the H-bonded XH group, and the proton affinity of the aromatic molecule's conjugate base.

Keywords
ci, spectra, infrared, molecules, aromatic, anion, chloride, between, interactions, complexes, _c6h5nh2, _c6h5oh, _c6h5ch3, GeoQUEST

Disciplines
Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Interactions between the Chloride Anion and Aromatic Molecules: Infrared Spectra of the Cl$^-$–C$_6$H$_5$CH$_3$, Cl$^-$–C$_6$H$_5$NH$_2$ and Cl$^-$–C$_6$H$_5$OH Complexes

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The Cl$^-$–C$_6$H$_5$CH$_3$, Cl$^-$–C$_6$H$_5$NH$_2$, and Cl$^-$–C$_6$H$_5$OH anion complexes are investigated using infrared photodissociation spectroscopy and ab initio calculations at the MP2/aug-cc-pVDZ level. The results indicate that for Cl$^-$–C$_6$H$_5$NH$_2$ and Cl$^-$–C$_6$H$_5$OH, the Cl$^-$ anion is attached to the substituent group by a single near-linear hydrogen bond. For Cl$^-$–C$_6$H$_5$CH$_3$, the Cl$^-$ is attached to an ortho-hydrogen atom on the aromatic ring and to a hydrogen atom on the methyl group by a weaker hydrogen bond. The principal spectroscopic consequence of the hydrogen-bonding interaction in the three complexes is a red-shift and intensity increase for the CH, NH, and OR stretching modes. Complexities in the infrared spectra in the region of the hydrogen-bonded XH stretch band are associated with Fermi resonances between the hydrogen-stretching vibrational modes and bending overtone and combination levels. There are notable correlations between the vibrational red-shift, the elongation of the H-bonded XH group, and the proton affinity of the aromatic molecule’s conjugate base.

1. Introduction

This paper is concerned with the properties of the Cl$^-$–C$_6$H$_5$CH$_3$, Cl$^-$–C$_6$H$_5$NH$_2$, and Cl$^-$–C$_6$H$_5$OH complexes as revealed through their infrared spectra in the hydrogen-stretching region and through ab initio calculations. Motivation for investigating these systems stems in part from the importance of interactions between simple ions such as Na$^+$, K$^+$, and Cl$^-$ and the phenyl, alkyl, amino, and hydroxyl functional groups in different biological contexts, including ion transport in membrane channels. Prompted by this significance, Lisy and co-workers have studied the dissociative photodetachment dynamics of the Cl$^-$–C$_6$H$_5$CH$_3$, Cl$^-$–C$_6$H$_5$CH$_2$Ar, Cl$^-$–C$_6$H$_5$NH$_2$, and Cl$^-$–C$_6$H$_5$OH•Ar anion complexes using infrared photodissociation spectroscopy and through ab initio calculations. 10,11 The infrared spectroscopic consequence of the hydrogen-bonding interaction in the three complexes is a red-shift and intensity increase for the CH, NH, and OH stretching modes. Complexities in the infrared spectra in the region of the hydrogen-bonded XH stretch band are associated with Fermi resonances between the hydrogen-stretching vibrational modes and bending overtone and combination levels. There are notable correlations between the vibrational red-shift, the elongation of the H-bonded XH group, and the proton affinity of the aromatic molecule’s conjugate base.

2. Experimental and Theoretical Methods

2.1. Experimental Technique. The vibrational predissociation spectra of the Cl$^-$–SBz complexes were recorded in a low-energy guided ion beam apparatus. 16–18 The machine consists of a cluster ion source, a primary quadrupole mass filter, an octopole ion guide, a secondary quadrupole mass filter, and a microchannel plate detector. The complexes were synthesized in an electron beam crossed supersonic expansion of argon (6 bar) seeded with traces of CCl$_4$ (as a Cl$^-$ precursor) and the SBz molecule of interest.

In all three cases, the Cl$^-$–SBz binding energy is likely to exceed the IR photon energy. For example, the binding enthalpy of Cl$^-$–C$_6$H$_5$OH has been determined as 109.0 ± 8.4 kJ mol$^{-1}$ (~9100 cm$^{-1}$). 12,13 Although to our knowledge, the binding enthalpies of Cl$^-$–C$_6$H$_5$CH$_3$ and Cl$^-$–C$_6$H$_5$NH$_2$ have not been reported, they almost certainly exceed those of Br$^-$–C$_6$H$_5$CH$_3$.

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TABLE 1: Scaled Hydrogen Stretch Frequencies for Cl−—C6H4CH3, Cl−—C6H4NH2, and Cl−—C6H6OH (in cm−1) with Infrared Intensities (km mol−1) Given in Bracketsa

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*a For Cl−—C6H4CH3, superscripts al and ar denote localization of the vibration on the aliphatic or aromatic CH groups, respectively. Asymmetric and symmetric vibrations are indicated by a and s, respectively.

and Br−—C6H4NH2 (36. ± 7.5 and 61.1 ± 7.5 kJ mol−1, respectively). So that we could monitor single IR photon absorption by cold complexes, we have probed argon-solvated species (Cl−—SBZ•Ar), monitoring Ar atom loss as a function of the infrared wavelength. The presence of a weakly attached Ar atom has been shown to have a minimal effect on the IR spectra of other anion complexes, the main consequence being a narrowing and slight shifting of the vibrational bands.

The parent Cl−—SBZ•Ar clusters were mass-selected by a quadrupole mass filter, turned through 90° by a quadrupole bender, and injected into the octapole ion guide. Here, the clusters were irradiated with the counter-propagating output of a Nd:YAG-pumped OPO/OPA system (Continuum Mirage 3000). Resulting fragment ions were selected by a second quadrupole mass filter and sensed by a microchannel plate/scintillator/photomultiplier detector. Wavelength calibration was achieved by measuring the output from the first stage of the OPO and the 532 nm output from the Nd:YAG laser using a pulsed wavemeter (HighFinesse WS-7).

2.2. Theoretical Methods. Optimized geometries and vibrational frequencies for the Cl−—C6H4CH3, Cl−—C6H6, and Cl−—C6H5OH complexes were calculated out at the Møller–Plesset second-order (MP2) level of theory, using Dunning’s aug-cc-pVDZ basis set.21 This method has previously been demonstrated as suitable for describing the structures and energetics of hydrogen-bonded complexes and clusters containing halide anions.22,23 Calculations utilized the Gaussian 03 suite of programs.24

Simulated infrared spectra of the complexes were generated by scaling the calculated harmonic frequencies using a factor determined from the experimental and calculated harmonic hydrogen stretch frequencies of the SBz monomer. Experimental vibrational frequencies for toluene, aniline, and phenol were taken from refs 25–27. The resulting scaling factors were 0.9503 for toluene, 0.9583 and 0.9482 for the NH and CH stretches of aniline, and 0.9602 and 0.9514 for the OH and CH stretches of phenol. To generate the simulated IR spectra, the calculated transitions were convoluted by Gaussians having widths of 6 cm−1. Scaled vibrational frequencies, intensities, and assignments for the three complexes are given in Table 1.

3. Results

3.1. Cl−—C6H4CH3. Theoretical Results. (a) Conformations and Dissociation Energy. A Cl− anion can interact with a toluene molecule either through aliphatic or aromatic hydrogen atoms, making it an interesting system to study the competition between different types of hydrogen bonding. Different conformations of the Cl−—C6H4CH3 complex, corresponding to stationary points on the potential energy surface (PES), were calculated at the MP2/aug-cc-pVQZ level of theory and are shown in Figure 1.

The global minimum energy structure (structure 1) has the Cl− attached to toluene by a double contact H-bond, through an ortho-hydrogen atom on the aromatic ring as well as a hydrogen atom on the methyl group. The dissociation energy corrected for vibrational zero-point energy (ZPE) is 45.4 kJ mol−1; correction for basis set superposition error by the method of Boys and Bernardi reduces the dissociation energy to 38.2 kJ mol−1. Interestingly, it appears that the H-bond to the aromatic ring is stronger than the one to the methyl group. Evidence for this is that the distance between the ortho-H atom and the Cl− ion is predicted to be 2.504 Å, whereas the distance between the methyl group H atom and the Cl− ion is 2.628 Å. Furthermore, the H-bonded ortho-CH bond on the ring is lengthened by 0.5%, whereas the H-bonded CH on the methyl group is lengthened by only 0.2%. Double-contact H-bonds between halides and solvent molecules have also been observed for the Cl−—HCOOH complex, in which both the OH and CH groups are attached to the Cl− anion and in the Cl−—C6H5Br, Br−—C6H5, and Cl−—C6H5 complexes where the halide anions are attached to two neighboring hydrogen atoms.10

There are several higher-energy stationary points for the Cl−—C6H4CH3 system; these are discussed in order of increasing energy. Starting with structure 1, rotation of the methyl group by 60° leads to structure 2, which is a first-order saddle point lying 3.2 kJ mol−1 higher in energy. Structure 3, in which the Cl− anion is attached to the ortho- and meta-hydrogen atoms of the aromatic ring, is a stable minimum lying 8.2 kJ mol−1 above structure 1. For this structure, rotation of the methyl group by 60° changes the energy by <0.1 kJ mol−1. Structure 4, in which the Cl− is attached to the meta- and para-hydrogen atoms, is a stable geometry lying 10.4 kJ mol−1 above structure 1. Structure 5, in which the Cl− is bound by a single H-bond to the para-hydrogen, lies 12.1 kJ mol−1 above structure 1. Finally, for structure 6, the Cl− ion is attached to the methyl group by three equivalent hydrogen bonds. This configuration is a second-
order saddle point (with a doubly degenerate vibrational mode with imaginary frequency). The predicted infrared spectra associated with the different stable minima are discussed below in relation to the experimental spectrum.

(b) Rotation of the Methyl Group. One can anticipate that the methyl torsional potential for \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3 \) will differ profoundly from that of \( \text{C}_6\text{H}_5\text{CH}_3 \) because the \( \text{Cl}^- \) anion is H-bonded to both the methyl group and the aromatic ring. To investigate the influence of the attached \( \text{Cl}^- \), we calculated the methyl torsional potentials for \( \text{C}_6\text{H}_5\text{CH}_3 \) and \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3 \) in the MP2/aug-cc-pVDZ level in relaxed scans along the methyl torsional angle \( \phi \). The resulting torsional energy curve are shown in Figure 2. The potential energy curve for the toluene monomer exhibits a very small barrier for methyl internal rotation (13 cm\(^{-1}\)) and a parallel minimum energy configuration (\( \phi = 0^\circ \)). Experimentally, toluene is found to have a 4.9 cm\(^{-1}\) barrier for internal rotation and a perpendicular minimum energy configuration (\( \phi = 90^\circ \)).\(^{30,31}\) As the torsional potential curve for \( \text{C}_6\text{H}_5\text{CH}_3 \) is extremely shallow and depends on rather subtle interactions, it is perhaps not surprising that the MP2/aug-cc-pVDZ calculations fail to predict the correct configuration. As expected, the torsional potential is significantly modified for \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3 \) because of the dual H-bonds between \( \text{Cl}^- \) and \( \text{H} \) atoms on the methyl group and the ring; the torsional barrier increases to 266 cm\(^{-1}\) and the hindering potential exhibits 3 equivalent minima.

Experimental Results. The photodissociation IR spectrum of \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3\cdot\text{Ar} \) is displayed in Figure 3, along with the simulated spectra based on the scaled MP2/aug-cc-pVDZ vibrational frequencies and intensities for the four stable structures (structures 1 and 3–5 in Figure 1). The experimental spectrum is dominated by an intense broad feature centered near 2970 cm\(^{-1}\), with weaker features occurring above 3000 cm\(^{-1}\) and below 2940 cm\(^{-1}\). The \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3\cdot\text{Ar} \) spectrum differs significantly from the spectrum of the jet-cooled \( \text{C}_6\text{H}_5\text{CH}_3 \) monomer recorded by Fuji et al.\(^{32}\) For \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3 \), the CH stretch band structure spans a range (2850–3075 cm\(^{-1}\)) that is slightly lower in frequency than for the toluene monomer (2870–3100 cm\(^{-1}\)). Most noticeably, the dominant feature in the \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3\cdot\text{Ar} \) spectrum is a broad feature centered near 2970 cm\(^{-1}\), with weaker features occurring above 3000 cm\(^{-1}\) and below 2940 cm\(^{-1}\). The \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3\cdot\text{Ar} \) spectrum is characterized by a broad peak at 2970 cm\(^{-1}\), which is slightly lower in frequency than the dominant peak in the toluene spectrum (3035 cm\(^{-1}\)). The differences are presumably due to the influence of the ionic H-bonds on the CH stretch vibrational frequencies.

Evidence for the structure of \( \text{Cl}^-\text{C}_6\text{H}_5\text{CH}_3 \) can be obtained by comparing the experimental and simulated infrared spectra in the CH stretch region. Inspection of Figure 3 shows that the...
A possible explanation for the low inversion barrier in Cl\textsuperscript{−} between structures 3 and 2 are 0.5 kJ mol\textsuperscript{−1}. A band at 2885 cm\textsuperscript{−1} would be expected to show a prominent methyl CH stretch in the experimental spectrum.

Figure 4. Stable conformers of Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}. Relative energies (in kJ mol\textsuperscript{−1}) are given for each conformer.

4 would be expected to show a prominent methyl CH stretch band at 2885 cm\textsuperscript{−1}, whereas structure 5 should be dominated by a band at 2935 cm\textsuperscript{−1} associated with stretching vibration of the H-bonded para-hydrogen atom. Although most of the ions probed experimentally probably have structure 1, it is possible that minor fractions of the population have the higher-energy structures 3–5. Therefore, it is conceivable that additional peaks in the experimental spectrum are associated with these less stable forms.

3.2, Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}. Theoretical Results. At the MP2/aug-cc-pVDZ level, Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} is found to have the three stable minima shown in Figure 4. The lowest-energy structure features a near-linear H-bond between the Cl\textsuperscript{−} and one amine hydrogen (structure 1; bond angle of 173.2\textdegree), similar to the calculated structure of the I\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} complex. This conformer has a ZPE corrected dissociation energy \(D_0 = 75.6\) kJ mol\textsuperscript{−1}, with BSSE correction reducing this to 68.5 kJ mol\textsuperscript{−1}. Although the association enthalpy of Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} has not been measured, the calculated \(D_0\) is bracketed by the experimental association enthalpies of F\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} (131.0 ± 8.4 kJ mol\textsuperscript{−1}) and Br\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} (61.1 ± 7.5 kJ mol\textsuperscript{−1}). There are two higher-energy structures. In the first (structure 2), which lies higher in energy by 44.1 kJ mol\textsuperscript{−1} than the global minimum by 44.1 kJ mol\textsuperscript{−1}.

The lowest-energy structure features a near-linear H-bond between the Cl\textsuperscript{−} and one amine hydrogen (structure 1; bond angle of 173.2\textdegree), similar to the calculated structure of the I\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} complex. This conformer has a ZPE corrected dissociation energy \(D_0 = 75.6\) kJ mol\textsuperscript{−1}, with BSSE correction reducing this to 68.5 kJ mol\textsuperscript{−1}. Although the association enthalpy of Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} has not been measured, the calculated \(D_0\) is bracketed by the experimental association enthalpies of F\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} (131.0 ± 8.4 kJ mol\textsuperscript{−1}) and Br\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} (61.1 ± 7.5 kJ mol\textsuperscript{−1}). There are two higher-energy structures. In the first (structure 2), which lies higher in energy by 44.1 kJ mol\textsuperscript{−1} than the global minimum by 44.1 kJ mol\textsuperscript{−1}.

The calculated barrier for the umbrella inversion of the amine group in Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} is 2.8 kJ mol\textsuperscript{−1}, compared with 6.0 kJ mol\textsuperscript{−1} for bare aniline (experiment: 6.3 kJ mol\textsuperscript{−1}).

The calculated barrier for the umbrella inversion of the amine group in Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} is 2.8 kJ mol\textsuperscript{−1}, compared with 6.0 kJ mol\textsuperscript{−1} for bare aniline (experiment: 6.3 kJ mol\textsuperscript{−1}). The rather low barrier for umbrella inversion in the complex is unexpected given that MP2/aug-cc-pVTZ calculations predicted a larger inversion barrier for Cl\textsuperscript{−}NH\textsubscript{3} compared to bare NH\textsubscript{3}. A possible explanation for the low inversion barrier in Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} is that the Cl\textsuperscript{−}\textsuperscript{−}N cloud repulsion is minimized for the planar configuration and the opportunity for a weak secondary H-bond between the ortho-CH group and the Cl\textsuperscript{−} is maximized.

The barrier for transferring the Cl\textsuperscript{−} from one H to the other on the NH\textsubscript{2} group is 17.2 kJ mol\textsuperscript{−1}, considerably higher than the 6.4 kJ mol\textsuperscript{−1} barrier for Cl\textsuperscript{−}NH\textsubscript{3}. This may be a consequence of the stronger intermolecular H-bond in the Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} complex compared to Cl\textsuperscript{−}NH\textsubscript{3}.

Experimental Results. The IR spectrum of the jet-cooled aniline monomer contains a series of aromatic CH stretch bands in the 3000–3120 cm\textsuperscript{−1} region and symmetric and asymmetric NH\textsubscript{2} stretch bands at 3423 and 3509 cm\textsuperscript{−1}, respectively.

The aromatic CH stretch bands and the NH\textsubscript{2} bands are of comparable intensity. In contrast, the IR spectrum for Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}, shown in Figure 5, is dominated by a strong peak at 2920 cm\textsuperscript{−1} that can be assigned to a red-shifted H-bonded NH stretch mode for structure 1 shown in Figure 4. The free NH stretch band appears as a small but unmistakable peak at 3475 cm\textsuperscript{−1}, approximately midway between the symmetric and asymmetric NH stretch bands of the C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} monomer (3466 cm\textsuperscript{−1}) is 546 cm\textsuperscript{−1}.

Several much weaker bands appear in the aromatic CH stretch region (3000–3100 cm\textsuperscript{−1}). The feature centered at 2970 cm\textsuperscript{−1} does not correspond to any band in the simulated spectrum and may represent a combination or overtone band deriving intensity through Fermi resonance with the strongly red-shifted NH stretch mode.

Comparison of the experimental spectrum and the simulated spectrum for structure 1 suggests that the scaled harmonic frequency for the H-bonded NH stretch mode (3073 cm\textsuperscript{−1}) overestimates the experimental value (2929 cm\textsuperscript{−1}).

3.3, Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}OH. Theoretical Results. The MP2/aug-cc-pVDZ calculations suggest that Cl\textsuperscript{−} prefers to bind to the hydroxy group of the C\textsubscript{6}H\textsubscript{5}OH molecule (structure 1, Figure 6). This structure has a ZPE-corrected dissociation energy of \(D_0 = 107.1\) kJ mol\textsuperscript{−1}, with BSSE correction reducing this to 99.3 kJ mol\textsuperscript{−1}. The calculated value compares reasonably well with the measured association enthalpy (109.0 ± 8.4 kJ mol\textsuperscript{−1}).

The OH bond is elongated from 0.968 Å for bare phenol to 1.013 Å for the complex. This significant elongation, which can be viewed as reflecting incipient proton transfer to the Cl\textsuperscript{−} anion, is also reflected in a large red-shift of 841 cm\textsuperscript{−1} in the scaled harmonic stretch frequency. The Cl\textsuperscript{−}···H intermolecular bond length (1.969 Å) is significantly shorter than that for Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3} (2.628 and 2.504 Å) and Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} (2.166 Å).

Figure 5. (a) Experimental infrared spectrum of Cl\textsuperscript{−}-C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}·Ar, and (b) simulated spectrum based on calculations at the MP2/aug-cc-pVDZ level. Arrows indicate symmetric and asymmetric NH\textsubscript{2} stretch bands for C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}. Scaled vibrational frequencies, intensities, and assignments are given in Table 1.
Experimental Results. The IR spectrum of the jet-cooled phenol monomer recorded by Yamada et al. contains an OH stretch band at 3657 cm$^{-1}$ in a region somewhat below where the calculations predict the H-bonded OH stretch should occur. These features are probably attributable to the OH stretch mode and neighbouring combination and overtone levels gaining IR intensity through Fermi resonance. If this is the case, the zero-order frequency for the H-bonded OH stretch mode can be estimated from the center of gravity of the bands in the 2550–2850 cm$^{-1}$ range. The resulting zero-order OH stretch frequency (2725 cm$^{-1}$) corresponds to a red-shift of ~930 cm$^{-1}$ with respect to the OH stretch band of the C$_6$H$_5$OH monomer (3657 cm$^{-1}$). As in the case of Cl$^-$–C$_6$H$_5$NH$_2$, it seems that the scaled harmonic frequency for the H-bonded OH stretch mode (2815 cm$^{-1}$) overestimates the experimental value, presumably because the frequency scaling does not adequately account for the extreme anharmonicity in the H-bonded XH stretch coordinate. This issue is addressed below.

4. Discussion

The calculations and infrared spectra described in the preceding section suggest that the Cl$^-$–C$_6$H$_5$CH$_3$, Cl$^-$–C$_6$H$_5$NH$_2$, and Cl$^-$–C$_6$H$_5$OH complexes all possess structures in which the Cl$^-$ is hydrogen bonded to a single hydrogen atom on the substituent group. In the case of Cl$^-$–C$_6$H$_5$CH$_3$, there is also a second, stronger H-bond with the ortho-hydrogen atom on the aromatic ring. Although for all three complexes, higher-lying isomers in which the Cl$^-$ anion is H-bonded to one or two hydrogen atoms on the phenyl ring are predicted, the barriers for conversion to the lowest-energy form are generally found to be small. For the lowest-energy form of all three Cl$^-$–SBz complexes, the principal spectroscopic consequence of the hydrogen-bonding interaction is a red-shift and intensity increase for the CH, NH, and OH stretching modes. Unfortunately, straightforward comparisons between the experimental and simulated spectra are complicated by Fermi resonances between the H-bonded XH stretch coordinate and bending overtones and combinations, particularly for Cl$^-$–C$_6$H$_5$CH$_3$ and Cl$^-$–C$_6$H$_5$OH. Nevertheless, in all three cases, there is clearly a systematic red-shift and intensity increase in vibrational modes associated with the H-bonded XH groups.

The Cl$^-$–SBz complexes can be considered as intermediates for the proton-transfer reaction

$$\text{Cl}^- + \text{HA} \rightarrow \text{HCl} + \text{A}^-$$

Because the proton affinity (PA) of Cl$^-$ (14.46 eV$^{39}$) is less than the PAs of C$_6$H$_5$CH$_3^-$, C$_6$H$_5$NH$_2^-$, and C$_6$H$_5$O$^-$ (16.45, 15.89, and 15.16 eV, respectively$^{39}$), the complexes consist essentially of a Cl$^-$ anion attached to a perturbed SBz molecule. Nevertheless, there is a degree of proton transfer from the SBz to the chloride anion, the extent of which is determined by the difference between the proton affinities (ΔPA) of the Cl$^-$ and the A$^-$ base. The degree of proton transfer is reflected in the magnitudes of the vibrational red-shift for the H-bonded XH group and elongation of the H-bonded XH bond.$^{40}$ The experimental red-shifts follow the expected trend, with Cl$^-$–C$_6$H$_5$CH$_3$ (large ΔPA) exhibiting the smallest red-shift and Cl$^-$–C$_6$H$_5$OH (small ΔPA) the largest.

The experimental frequencies for the H-bonded NH and OH stretch vibrations of Cl$^-$–C$_6$H$_5$NH$_2$ and Cl$^-$–C$_6$H$_5$OH are somewhat lower than the scaled calculated harmonic frequencies.
Figure 8. One-dimensional NH/OH stretch potential energy curves (calculated at the MP2/aug-cc-pVDZ level) for (a) C6H5NH2, (b) Cl–C6H5NH2, (c) C6H5OH, and (d) Cl–C6H5OH. In each case, the lowest three energy levels and associated wave functions are shown.

(see Figures 5 and 7). A likely source of the discrepancy is anharmonicity in the H-bonded NH stretch coordinate not fully accounted for by frequency scaling. To investigate this possibility, we calculated one-dimensional potential energy curves (at the MP2/aug-cc-pVDZ level) for the H-bonded NH stretch motion (with remaining coordinates fixed). Plots for both the free SBz molecule and the corresponding Cl–SBz complex appear alongside one another in Figure 8, highlighting the influence of the attached Cl–ion. The distortion of the potential energy curves for Cl–C6H5NH2 and Cl–C6H5OH is quite evident, illustrating the marked delocalization of the shared proton.

Frequencies for the hydrogen stretch vibrations associated with the one-dimensional potential curves were calculated using Level 7.4, assuming that the vibration involved only motion of the H-bonded hydrogen atom. The effective mass of the oscillator was assumed to be 1 amu. The first three vibrational levels are superimposed on the potential curves in Figure 8. For Cl–C6H5NH2, the NH stretch transition is calculated to lie at 2845 cm−1, comparing favorably with the experimental value (2920 cm−1). For Cl–C6H5OH, the OH stretch frequency is calculated to lie at 2400 cm−1, around 415 cm−1 below the scaled harmonic frequency, and indeed below the series of bands apparent in the experimental spectrum between 2600 and 2800 cm−1. This raises the possibility that the OH stretch band occurs below 2550 cm−1, beyond the wavelength range of the OPO used in this work. However, it is also feasible that the reduced mass used in the 1D vibrational frequency calculations is slightly too high, leading to an overestimation of the stretching frequency.

One might expect that there should be similarities between the Cl–SBz complexes (Cl–C6H5CH3, Cl–C6H5NH2, Cl–C6H5OH) and complexes of Cl− and the second-row hydride molecules (Cl−CH3, Cl−NH3, and Cl−H2O), which have also been studied using infrared spectroscopy and through ab initio calculations. In effect, the two sets can be distinguished as CH3, NH2, or OH functionalities associated with either an H or C6H5 subgroup. The extent of proton transfer to the Cl− anion can be expected to be larger for the SBz molecules, because the PAs for C6H5CH3−, C6H5NH−, and C6H5O− (16.45, 15.89, and 15.16 eV) are lower than those of CH−, NH−, and OH− (18.13, 17.49, and 16.92 eV). This is reflected in the magnitudes of the vibrational red-shifts and the elongation of the XH bond (calculated at the MP2/aug-cc-pVDZ level), both of which are plotted against ∆PA in Figure 9. Note that for Cl−C6H5CH3, it is difficult to ascertain the magnitude of the red-shift because of the complexity of the spectrum and because both the aromatic and aliphatic CH stretch modes are affected by H-bonding. It is obvious from Figure 9 that the Cl−SBz complexes are associated with larger red-shifts and XH bond elongations than the complexes containing the corresponding second-row hydride molecule. For both sets of complexes, there is a near-linear correlation between ∆PA and the vibrational red-shift and the XH bond elongation.

Last, we consider the effect of the attached Ar atom. Although in each case the experimental spectrum does not provide direct information on the position of the Ar atom, presumably because the Ar···Cl− bond (D0 = 523 cm−1; ref39) is comparable in strength with Ar···aromatic bonds (for example, D0 = 314 ± 7 cm−1 for C6H6·Ar; ref40), the Ar atom is positioned so as to maximize the interaction with both the Cl− and the SBz subunit. For Cl−C6H5CH3·Ar, Alberti et al. found that the most favorable location for the Ar atom is midway between the benzene ring and the Cl−, so that it is stabilized by interactions with both the anion and the Bz molecule.52 The situation is probably similar for the Cl−SBz complexes.

5. Summary

Infrared spectra have been recorded for Cl−C6H5CH3·Ar, Cl−C6H5NH2·Ar, and Cl−C6H5OH·Ar using vibrational predissociation spectroscopy. Accompanying ab initio calculations suggest that the lowest-energy conformers for Cl−C6H5NH2 and Cl−C6H5OH have the Cl− bound to a single hydrogen atom of the substituent group. In the case of Cl−C6H5CH3, the Cl− is hydrogen bonded to an ortho-hydrogen atom on the ring and to a hydrogen atom on the methyl group. Complexities in the infrared spectra are postulated to arise from Fermi resonances between the H-bonded XH stretch and overtone and...
The XH group (Cl both the vibrational red-shift and the elongation of the H-bonded proton affinity of the aromatic molecule’s conjugate base and both the vibrational red-shift and the elongation of the H-bonded XH group (Cl−C6H5CH3 < Cl−C6H5NH2 < Cl−C6H5OH).

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References and Notes

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