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LETTERS

Resolving Discrepancies between Theory and Experiment: IR Spectrum of the Proton-Shared HBr:Pyridine Complex

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The computed MP2/6-31+G(d,p) structure of the HBr:pyridine complex and the computed harmonic and experimental spectra of this complex agree that HBr:pyridine is stabilized by a proton-shared hydrogen bond. However, differences are evident between the computed and experimental spectral patterns with respect to the frequencies and intensities of strong bands. Solution of a one-dimensional nuclear vibrational equation along the normal coordinate mode allows for an estimation of an anharmonicity of the proton-stretching motion. When an anharmonic stretching force constant is used to recompute the spectrum, excellent agreement is found between theory and experiment.

Introduction

In our previous papers,[1,2] we presented the results of MP2/6-31+G(d,p) calculations carried out on a series of complexes formed between the hydrogen halides HF, HCl, and HBr and a set of 4-substituted pyridines (HX:4-(*R*)-pyridine). The HBr:pyridine complex included in this study was found to have C_{2v} symmetry, with a short intermolecular Br−N distance of 2.958 Å, a long Br−H distance of 1.802 Å, a long N−H distance of 1.156 Å, and a vibrational spectrum characteristic of a complex stabilized by a proton-shared hydrogen bond. Subsequent experimental studies of HBr:pyridine in an Ar matrix at 10 K also found an IR spectrum characteristic of a proton-shared hydrogen bond. These spectra feature multiple strong bands at frequencies below 1800 cm^{-1}. However, there are discrepancies between the computed and experimental spectral patterns with respect to both the frequencies and the relative intensities of the strong bands. It is the purpose of this paper to identify the source of these discrepancies and to resolve them.

Methods

The structure of HBr:pyridine was fully optimized with correlation at second-order many-body Møller-Plesset perturbation theory (MBPT(2) = MP2][3-6] with the 6-31+G(d,p) basis set.[7-10] The vibrational spectrum was computed within the harmonic approximation. In hydrogen-bonded complexes with traditional hydrogen bonds, the MP2/6-31+G(d,p) level of theory has been shown to produce vibrational frequency shifts that are in reasonable agreement with experiment.[11]

Because the hydrogen-bonded proton executes large amplitude vibrational motion in this complex, the true proton-stretching coordinate may be very anharmonic. To investigate this, single-point MP2/6-31+G(d,p) calculations were carried out to generate the potential energy curve along the normal coordinate corresponding to the harmonic stretching mode at 1561 cm^{-1}. On the basis of this curve, approximate anharmonic

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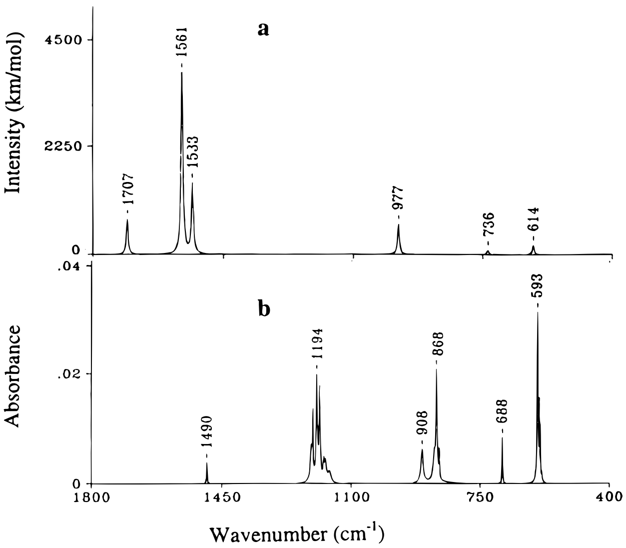

Figure 1. Computed MP2/6-31+G(d,p) harmonic spectrum (a) and the experimental Ar matrix IR spectrum (b) of the HBr:pyridine complex extracted from the original experimental spectrum of the matrix containing the pyridine and HBr monomers and the complex. See ref 17.

frequencies and a force constant for this mode were obtained by numerical solution of the one-dimensional nuclear Schroedinger equation.[12] The entire vibrational spectrum of HBr:pyridine was then recomputed using the PACK program[13] with the anharmonic force constant for the hydrogen-bonded proton stretch, with no other adjustments being made. All of the MP2 calculations were carried out at the Ohio Supercomputer Center using the Gaussian 94 suite of computer programs.[14]

An FTIR Nicolet 740 spectrometer and closed helium cryostat were used to record the experimental spectrum of HBr:pyridine. A gaseous mixture of Ar, HBr, and pyridine in a ratio of about 2500:1:1 was deposited on the cold window of the cryostat at about 10 K. The initial IR spectrum shows bands originating primarily from the monomers, with only a small amount of complex. Subsequent annealing at about 30 K allows diffusion of the monomers through the matrix, leading to the formation of the 1:1 HBr:pyridine complex. The matrix was cooled back to 10 K, and its spectrum was recorded. In this spectrum the absorption bands related to the 1:1 HBr:pyridine complex show a significant increase in intensity relative to the monomer bands. The experimental spectra of monomers and complex were analyzed using the SpectraCalc and Grams programs.[15,16] Integrated intensities and relative concentrations of all species were determined. Details of the experimental procedure and discussion and interpretation of the experimental matrix spectra of monomers and complex are given elsewhere.[17]

Results and Discussion

The computed harmonic and the experimental IR spectra of the HBr:pyridine complex are shown in Figure 1. Evident in both spectra are multiple intense bands below 1800 cm^{-1}. Analysis of the computed spectrum shows that these bands arise from coupling between the hydrogen-bonded proton stretching mode, which is dramatically shifted to low frequency, and local modes of the pyridine ring, which also have a_1 symmetry and similar frequencies. This coupling of modes is characteristic of the spectra of HX:4-(*R*)-pyridine complexes with proton-shared hydrogen bonds.[1,2] However, it is also evident from Figure 1 that there are differences between the computed harmonic spectrum and the experimental spectrum in terms of both frequencies and relative intensities of the strong bands. There are two possible reasons for these differences: an environmental effect due to the Ar matrix or the failure of the harmonic approximation to adequately describe the proton-stretching vibration.

The matrix effect has been investigated by optimizing the structure of the HBr:pyridine complex in the presence of two Ne atoms. The complex HBr:pyridine:2Ne also has C_{2v} symmetry, with the Ne atoms above and below the plane of the pyridine ring. Our preliminary computational studies indicated that Ar and Ne have similar effects on the structure and spectra of hydrogen-bonded complexes, so Ne was used to reduce the computational cost. The optimized structure of HBr:pyridine:2Ne was essentially identical to that of HBr:pyridine. Since the correlation between structure and spectra is well established in these systems,[1,2] the spectrum of HBr:pyridine:2Ne is anticipated to be essentially identical to that of HBr:pyridine. Hence, it is unlikely that the Ar matrix is responsible for the difference between the computed and experimental spectra shown in Figure 1.

The most likely cause of this discrepancy seems to be the harmonic approximation. In order to estimate the magnitude

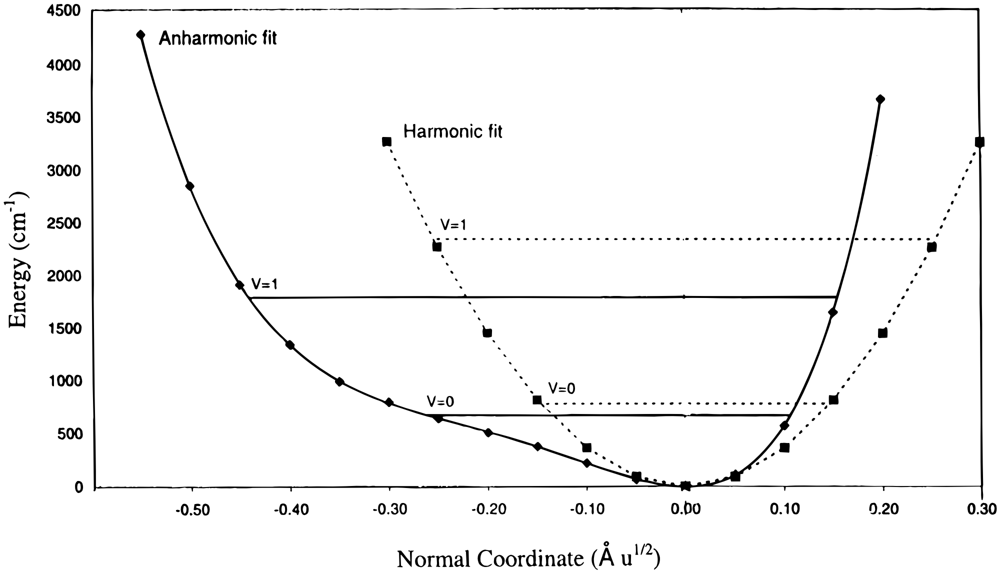

Figure 2. Potential curve for proton motion along the normal coordinate for the band at 1561 cm^{-1} and the $v = 0$ and $v = 1$ vibrational levels for this curve (solid line). The harmonic curve and vibrational levels are shown for comparison (dashed line).

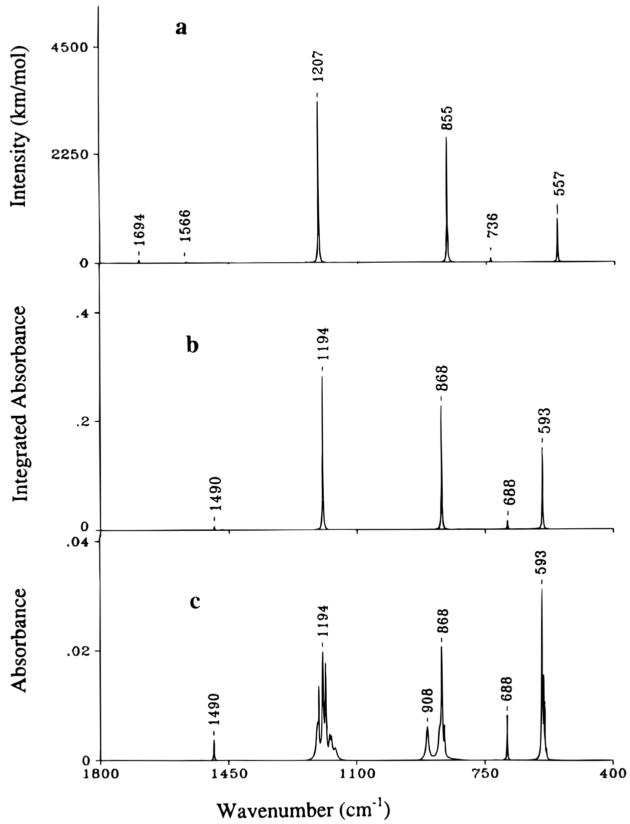

Figure 3. Recomputed HBr:pyridine spectrum using the anharmonic proton stretching force constant (a), the experimental integrated intensity sum spectrum (b), and the experimental spectrum (c).

of the anharmonicity of the proton-stretching vibration in HBr:pyridine, single-point MP2/6-31+G(d,p) energies were computed along the vector describing the normal coordinate motion for the band at 1561 cm^{-1}. These energies were then fitted by a quartic polynomial to give the curve shown in Figure 2. For comparison, the harmonic curve for the same normal mode is also shown. As seen in this figure, the proton motion is strongly anharmonic.

A one-dimensional nuclear vibrational equation was solved following the procedure suggested by Somorjai and Hornig[13] using this computed anharmonic potential. Anharmonic eigenvalues were obtained, and these are compared with the harmonic in Figure 2. While the harmonic and anharmonic zero-point vibrational energies are similar, the $v = 1$ anharmonic level is significantly lower than the harmonic level. From these data, the ratio of the $v = 0 \rightarrow v = 1$ anharmonic and harmonic vibrational transition energies can be obtained. $v_{0\rightarrow1}$(anharmonic)/$v_{0\rightarrow1}$(harmonic) ≈ 0.72 This value was then used to adjust the proton-stretching force constant. k(anharmonic)/k(harmonic) $= 0.72^2 = 0.52$ The three internal coordinate force constants (NHs, BrHs, and their interaction constant in the notation of ref 17) obtained from the harmonic calculation were then multiplied by 0.52, and the spectrum of HBr:pyridine was recomputed.[13] No adjustments were made to any other force constants. The recomputed HBr:pyridine spectrum is shown in Figure 3a and can be compared with the experimental matrix spectrum shown in Figure 3c. Figure 3b also shows an experimental integrated intensity sum spectrum obtained by combining the integrated intensities of weaker bands in the vicinity of a strong band into a single band.[17] As seen, the agreement among the three spectra is remarkable.

Conclusions

Both theory and experiment agree that the HBr:pyridine complex has a proton-shared hydrogen bond. However, differences are apparent between the computed harmonic and the experimental frequencies and relative intensities of characteristic strong bands in the spectrum associated with the hydrogen-bonded proton-stretching motion. These differences are shown to arise from the inadequacy of the harmonic treatment of proton motion. Solving a one-dimensional vibrational problem using the potential along the normal proton-stretching coordinate provides an estimate of the anharmonicity correction. Applying this correction leads to excellent agreement between the recomputed HBr:pyridine spectrum and the experimental spectrum.

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