Electric Field Effect on Condensed-Phase Molecular Systems. VI. Field-Driven Orientation of Hydrogen Chloride in an Argon Matrix

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ABSTRACT: The orientation state of hydrogen chloride (HCl) molecules in a solid argon matrix was reversibly controlled by applying an external electric field of up to $4 \times 10^8$ V·m$^{-1}$ using the ice film capacitor method. The rovibrational transitions of the field-oriented HCl were measured by reflection absorption infrared spectroscopy with $p$-polarized light. Upon application of the external field, free rotation of HCl inside the matrix gradually changed to perturbed rotation and then to a pendular state harmonically bound in the Stark potential well. Further increase in the field strength increased the degree of dipole alignment along the field direction, approaching an asymptotically perfect orientation of the molecules with an average tilt angle of $<30^\circ$ at a field strength above $1 \times 10^8$ V·m$^{-1}$.

I. INTRODUCTION

Electrostatic interactions between the permanent dipole moment of polar molecules and an external electric field can be used to orient the molecules along the direction of the field. If the field is strong enough to create a barrier to the free rotation of the molecules, they undergo a hindered rotation or pendular motion with their permanent dipole moments oriented preferentially along the field direction.1−12 This method of brute force orientation has been widely used to orient polar molecules seeded in supersonic beams for the study of directional states,1,4−13 photodissociation dynamics,14−17 and reactive collisions of spatially oriented molecules.18,19 One of the strongest orientations achieved by this method was that of (HCN)$_3$ in molecular beams.8 A large dipole moment (10.6 D) and a small rotational constant (0.0156 cm$^{-1}$) of this chain molecule at the low rotational temperature ($\leq 2$ K) provided favorable conditions for the efficient alignment of the molecule. As the electric field strength was increased, it was observed that the infrared (IR) spectrum of the molecules evolved from one with normal P and R branch structures corresponding to the freely rotating state of a linear molecule, into one characteristic of pendular states trapped in the Stark potential in the high-field limit ($3 \times 10^8$ V·m$^{-1}$).8,9

Despite the successful demonstration of the brute force orientation of a few highly polar molecules in supersonic beams, it remains an experimental challenge to obtain a high degree of orientation polarization for a more general class of polar molecules. The key to the success of brute force orientation is a strong electric field and a low rotational temperature. For this purpose, Shin et al.20 reported the ice film capacitor method that can apply an electric field of up to $\sim 4 \times 10^8$ V·m$^{-1}$, higher than that achievable by conventional metal plate capacitors, to a frozen molecular film inside a vacuum chamber. Recently, Park et al.21 applied this method to matrix-isolated molecules and showed that formaldehyde molecules that are frozen in position in a solid argon (Ar) matrix are reoriented by the applied field along the field direction. In the present study, we have extended this approach to hydrogen chloride (HCl) molecules isolated in an Ar matrix (HCl@Ar). Different from the case of formaldehyde, the HCl molecule rotates almost freely inside the Ar matrix, showing the P and R branch structure of a linear molecule in IR spectrum.22 The rotational constant of the matrix-isolated HCl in its electronic ground state is 8.5−9.0 cm$^{-1}$, close to that of gas-phase HCl (10 cm$^{-1}$).23,24 As the rotational constant of HCl is larger than that of (HCN)$_3$ by 2−3 orders of magnitude, a much stronger field is needed to induce the pendular state of HCl.4−6 The present study demonstrates that a strong external field can change the rovibrational state of HCl from a free rotor to the pendular state and then eventually to full asymptotic orientation along the field direction as the field strength increases from 0 to $4 \times 10^8$ V·m$^{-1}$.

II. EXPERIMENTAL METHODS

The experiments were performed in an ultrahigh-vacuum (UHV) chamber,25 which was equipped with a low-energy Cs$^+$ ion gun, a Kelvin work-function probe, a Fourier transform infrared (FTIR) spectrometer, and a quadrupole mass spectrometer. The Pt(111) metal substrate was cooled to $\sim 7$ K by a closed-cycle He refrigerator. Frozen molecular films were grown on the Pt(111) surface by sequential deposition of the gases through leak valves. A tube doser was used to introduce the HCl gas close to the Pt(111) surface to minimize the contamination of the chamber wall. Ar and H$_2$O gases were deposited by backfilling the chamber. Ar (99.999%) and HCl (Sigma-Aldrich, >99%) gases were used as received in...
commercial gas cylinders. H$_2$O was purified by freeze–pump–thaw cycles.

The thicknesses of the constituent molecular films in the sample were estimated from temperature-programmed desorption (TPD) measurements. The thickness of the H$_2$O film was determined by comparing its TPD peak area with that of the H$_2$O monolayer formed on Pt(111). The TPD peak area of the Ar film was compared with an H$_2$O film of known thickness by considering the different ionization cross sections of the gases in mass spectrometric detection. The thickness of 1 monolayer (ML) of amorphous solid water is 5.5 Å and that of solid Ar is 5.7 Å, as estimated from the densities of these molecular films at 7 K. An electric field was applied across the HCl@Ar sample by using the ice film capacitor method. An alkali metal ion gun (Kimball Physics) was used to deposit Cs$^+$ ions at a low incidence energy uniformly on the surface of the H$_2$O layer of the ice film capacitor. The voltage developed across the ice film capacitor was measured by a Kelvin work-function probe. The field strength across the HCl@Ar film was estimated using eq 1.

$$F = \frac{V}{d_{\text{Ar}} + d_{\text{H}_2\text{O}} \frac{\varepsilon_{\text{Ar}}}{\varepsilon_{\text{H}_2\text{O}}}}$$  \hspace{1cm} (1)$$

where $V$ is the capacitor voltage, as measured by a Kelvin probe, and $d_{\text{Ar}}$ and $d_{\text{H}_2\text{O}}$ are the corresponding film thicknesses. The parameters $\varepsilon_{\text{Ar}}$ and $\varepsilon_{\text{H}_2\text{O}}$ are the relative permittivities of each film and have the values of 1.6 and 2.0, respectively. The external field strength calculated by eq 1 can be converted to the local field strength by including the contributions of the cavity and reaction fields, according to the classical electrostatic model and Onsager reaction field theory. This conversion procedure has been described in detail previously. It leads to a local field correction factor of 1.16 for HCl inside a spherical cavity of the Ar matrix, as calculated from reported physical parameters.

RAIRS measurements were performed at a grazing angle of 84° using a FTIR spectrometer equipped with a mercury cadmium telluride detector. The IR beam was p-polarized using a wire grid polarizer placed in the incident beam path, and the RAIRS spectra were scanned 2304 times at a spectral resolution of 1 cm$^{-1}$.

**III. RESULTS AND DISCUSSION**

We constructed an ice film capacitor device containing an HCl@Ar sample as shown in the inset of Figure 1. First, an Ar film was laid on a Pt(111) substrate inside a vacuum chamber with a thickness of 45 ± 2 ML as the spacer layer. Then, an HCl@Ar film of thickness ranging from 90 ± 3 to 450 ± 16 ML was grown by codeposition of HCl and Ar gases at partial pressures of a predetermined ratio using separate dosing facilities. Another Ar spacer layer (45 ± 2 ML) was placed on top of the HCl@Ar film. Finally, the sample was capped with an amorphous H$_2$O film having a thickness of 27 ± 1 ML. The temperature of the Pt substrate was maintained at ~7 K during sample preparation. The film thicknesses and the Ar/HCl molar ratio in the HCl@Ar matrix were determined by performing thermal desorption mass spectrometry experiments. The reflection absorption infrared (RAIR) spectra of the HCl@Ar samples are shown in Figure 1. The spectrum in Figure 1a shows three major peaks at 2888, 2818, and 2787 cm$^{-1}$, which are assigned to the HCl monomer, dimer, and trimer in the HCl@Ar sample as shown in the inset of Figure 1. First, the R(0) peak at 2888 cm$^{-1}$ was

![Image](https://example.com/image1.png)

**Figure 1.** RAIR spectra of HCl in an Ar matrix at ~7 K in the absence of an external electric field. (a) Ar/HCl molar ratio of the HCl@Ar sample was 340:1. (b) Ar/HCl molar ratio was 870:1. The HCl@Ar films in the two samples were of different thickness, 90 ± 3 ML (a) and 450 ± 16 ML (b), in order to compensate for the different HCl concentrations of the samples. The inset shows a schematic drawing of the ice film capacitor structure containing an HCl@Ar film. The HCl monomer, dimer, and trimer peak positions are marked by dashed lines. Typical IR spectra have significant slopes due to multiple reflections in a thin film sample. Such baselines have been subtracted in the spectra displayed in the figure.

An electric field was applied across the HCl@Ar sample by charging the H$_2$O surface of the ice film capacitor with Cs$^+$ ions. This led to the Pt metal surface becoming negatively charged by induced electrons, as depicted in Figure 2. The spectral changes resulting from the applied electric field are displayed in Figure 2. First, the R(0) peak at 2888 cm$^{-1}$ was

![Image](https://example.com/image2.png)
blue-shifted in the presence of the applied field. Also, its intensity increased with increasing field strength and disappeared almost completely at a field strength above \( \sim 6 \times 10^7 \text{ V} \cdot \text{m}^{-1} \) (between the green and blue spectra). Second, a new peak appeared at 2871 cm\(^{-1}\), which corresponded to the fundamental vibrational band center of HCl. The band center position is estimated from the R and P branch structures of HCl in an Ar matrix that appear at higher temperatures.\(^\text{25,35}\) The shoulder structure of this peak at \( \sim 2868 \text{ cm}^{-1} \) corresponds to the band center of the \( ^7\text{Cl} \) isotopomer. The intensity of the band center peak grew stronger with increasing field strength, and its position exhibited a vivid red-shift above \( \sim 8 \times 10^7 \text{ V} \cdot \text{m}^{-1} \). Third, another new (N) peak appeared at 2855 cm\(^{-1}\) with a lower intensity than that of the band center.

The appearance of the band center and the blue-shift of the R(0) peak in Figure 2 indicates that the applied field gradually changes the free rotation of HCl to pendulum motion bound by the electrostatic interaction potential of the dipole with the field. The field-induced change of a free rotor to a pendular state has been demonstrated previously, for example, for HCl seeded in supersonic molecular beams\(^\text{25,6}\) and a linear (HCN), complex in supersonic molecular beams.\(^\text{25} \) These studies showed that the spectral change of linear molecules from a free rotor to pendular state is characterized by the appearance of a vibrational band center and blue- and red-shifts of the R and P branches, respectively, away from the band center. These changes occur when the polarization of the infrared light and the applied field are in the same direction,\(^\text{25,61}\) as in the present experimental geometry. The similar behavior is observed in Figure 2, i.e., the coexistence of the R(0) and the band center peaks, and the blue-shift of the R(0) peak. These changes indicate that HCl rotation is perturbed by the applied field. The quantum mechanical description for the transition from a linear free rotor to pendular state has been previously given in the literature,\(^\text{6,8} \) which may also apply to the present spectral changes.

When a molecule is situated in the Stark potential generated by an electric field along the z-direction (in laboratory space), the rotational quantum number \( J \) of the molecule is no longer a good quantum number, but the z-projection quantum number \( M \) is. The selection rule for the absorption of polarized light in the z-direction is \( \Delta M = 0 \). In this case, there are two allowed rovibrational transitions for HCl in the perturbed rotor state at the low temperature (\( \sim 7 \text{ K} \)), going from the ground state \( (J_p = 0, M_p = 0) \) to the \( J_p = 1, M_p = 0 \) and \( J_p = 0, M_p = 0 \) states, which produce the R(0) and band center peaks, respectively. The designation \( J_p \) (subscript \( F \) for field) is used here instead of \( J \), because \( J \) is no longer a quantum number. As the field becomes even stronger (\( \sim 6 \times 10^7 \text{ V} \cdot \text{m}^{-1} \)), the molecules become essentially harmonically bound in the Stark potential with its dipole oriented preferentially along the field direction, and the R(0) structure fades away. In this pendular state, the degree of dipole alignment of HCl molecules along the field increases with the increase in the applied field strength. Meanwhile, the blue-shift of R(0) in the perturbed rotor regime is caused by the Stark effect on the rotational states, which stabilizes the rotational ground state more than the first excited state, as calculated in the previous reports.\(^\text{7,36}\)

The reorientation energy of HCl in an electric field \( (u = \mu F) \) is, for instance, roughly 130 J mol\(^{-1}\) at \( F = 6 \times 10^7 \text{ V} \cdot \text{m}^{-1} \). Since this energy is substantially larger than the thermal energy (about 60 J mol\(^{-1}\)) at the matrix temperature, it is reasonable that a majority of the HCl molecules are trapped in the Stark potential with its dipole lying along the field direction. Indeed, the R(0) structure almost disappeared at this field strength. In this regime, the intensity of the band center peak increased monotonously with increasing field strength, which indicated an increase in the light absorbance because of a further alignment of the molecular axis along the direction of light polarization, which is parallel to the field direction. The rate of increase of the peak intensity diminished above \( \sim 2 \times 10^8 \text{ V} \cdot \text{m}^{-1} \), as the molecules approached asymptotically toward a perfect alignment with the field direction.

The red-shift of the band center of the dipole-aligned HCl molecules, appearing at high fields in Figure 2, occurs reversibly with respect to an increase or decrease in the field. This behavior is plotted in the upper panel of Figure 3, which shows a linear relationship between the reversible peak shift and the field strength in the range of \( 6 \times 10^7 - 4 \times 10^8 \text{ V} \cdot \text{m}^{-1} \). The peak shift can be explained by the vibrational Stark effect of field-oriented HCl molecules (eq 2).

\[
\Delta \nu = -\frac{1}{hc}\left(\Delta \mu \cdot \text{F} + \frac{1}{2} \text{F} \cdot \Delta \alpha \cdot \text{F} + \ldots \right)
\]

(2)

The Stark frequency shift \( (\Delta \nu) \) is proportional to the vibrational Stark coefficient (or Stark tuning rate; \( \Delta \mu \)) and the field component in the direction of the H–Cl bond to a first approximation. The second-order term related to the differential polarizability \( (\Delta \alpha) \) usually produces only a small effect on the frequency shift at the present field strength.\(^\text{38,59}\) The unidirectional frequency shift appears because of the field-orientation of the molecules. In contrast, for randomly orientated molecules, the Stark shifts of the oscillators on ensemble average give rise to spectral broadening rather than a unidirectional frequency shift.\(^\text{25,58}\) The plot shows that the data points fall nicely into a straight line above \( 6 \times 10^7 \text{ V} \cdot \text{m}^{-1} \). As
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Figure 3. (Top) Plot of the vibrational Stark shift of the vibrational band center of HCHCl vs electric field. Data points obtained from five different samples with varying Ar/HCl ratios, (100–400):1, are shown overlapped. Black squares indicate the measurements as the field increases and red squares as the field decreases. The slope of the plot in the linear region yields the vibrational Stark coefficient (see text). (Bottom) A plot of the full width at half-maximum (fwhm) of the band center peak of HCHCl vs electric field. Two Lorentzian curves with an equal fwhm are used to deconvolute the HCHCl and HCHCl peaks (inset); the black line is the raw spectrum, the red lines are the Lorentzian curves, and the red dashed line is the summation of the two Lorentzian curves. The vertical dotted line marks the field strength (6 × 10^7 V·m^−1) at the minimum fwhm.

the magnitude of the frequency shift depends on the angle between the directions of the molecular dipole and the applied field, \( \Delta \nu = |\Delta \mu| F \cos \theta \), the observed linearity with reliability >85% indicates that the average tilt angle of the molecules from the field axis is <30°. This indicates that the HCl molecules asymptotically approach perfect alignment with the field. To compare, the degree of field orientation observed in previous experiments is 52° for ICl at \( F = 2 \times 10^7 \) V·m^−1 and 16° for (HCN) at 3 × 10^6 V·m^−1 in terms of the average tilt angle from the field direction. The vibrational Stark coefficient can be estimated from the linear slope of the plot in Figure 3. For an accurate determination of \( \Delta \mu \), the actual field strength that the HCl molecule experiences inside the matrix needs to be determined. This local field strength is estimated by including the contributions of the cavity and reaction fields, as mentioned in Section II, which gives the local field correction factor, \( f = 1.16 \), for HCl in the Ar matrix. Then, the vibrational Stark coefficient is calculated as \( \Delta \mu = \Delta \nu / (f F_{ext}) = 2.3 \) (±0.1) cm^−1/(10^8 V·m^−1) (or 0.14 D). The slight bend in the plot at lower fields (<6 × 10^7 V·m^−1) is most likely caused by the random orientation of the molecules.

The lower panel of Figure 3 plots the fwhm of the band center peak of HCHCl as a function of the field strength. The fwhm was estimated by deconvoluting the spectral shape into two Lorentzian peaks corresponding to HCHCl and HCHCl. The fwhm decreased when the field strength was increased from 1.6 × 10^7 to 6 × 10^7 V·m^−1 but then increased at higher fields. It is worth noting that the minimum fwhm (1.4 cm^−1) observed at 6 × 10^7 V·m^−1 was limited by the instrumental spectral resolution, implying that the natural peak width could be narrower. The broad width observed at the lowest examined field strength (1.6 × 10^7 V·m^−1) could be attributed to the vibrational Stark broadening of the peak before field alignment occurred. The vibrational Stark shifts of the individual HCl molecules in random directions (rotors) contributed to the broadening of the peak width, although the magnitude of the Stark frequency shift for the individual molecules was small at this low field. As the field increased, the molecules become oriented, and at the same time, the Stark shift of the individual molecules also increased. The combined effects may lead to a momentary decrease in the fwhm with a red-shift of the peak position, which is shown in the lower and upper panels of Figure 3, respectively, in the region of 1.6–6 × 10^7 V·m^−1.

Therefore, the observed decrease in the fwhm lends additional support to the HCl rotor for change to an oriented, pendular state under the field. Above 6 × 10^7 V·m^−1, the peak width increases again with increasing field, despite a higher degree of molecular alignment. A plausible explanation for this phenomenon is the inhomogeneous broadening of the peak, which originates from local variations in the reaction field strength inside the matrix. The reaction field increases with the increase in external field strength because of their mutual feedback nature. This also increases the extent of variation in the reaction field strength at different local environments of the matrix as the external field increases. As a result, the inhomogeneous broadening can increase at a higher field.

To explore the origin of the new (N) peak at 2855 cm^−1, which appeared with a lower intensity than the band center peak (Q) when the external field was applied (Figure 2), we measured the changes in these peak intensities with the change in the HCl/Ar molar ratio of the sample. Figure 4 shows the absorbance ratio of N and Q peaks as a function of the HCl/Ar ratio. The N peak appeared with an observable intensity when the HCl/Ar molar ratio exceeded about 0.0013, which is...
marked by an arrow on the horizontal axis of the figure. The N/Q absorbance ratio increased roughly proportional to the HCl/Ar molar ratio above this threshold value. Because the Q peak increased linearly with HCl density in the matrix, the plot indicated a quadratic increase of the N peak intensity with HCl density. This behavior suggests that the N peak most likely originates from HCl dimers, whose population grows quadratically with respect to HCl density, rather than HCl monomers. However, it is not clear whether this peak comes from intact HCl dimers or field-induced dissociation of HCl dimers. In either case, this dimeric species is different from the ordinary HCl dimers that produce the peak at 2818 cm\(^{-1}\) in Figure 1.

IV. CONCLUSION

The externally applied field can change the rovibrational states of isolated HCl molecules in the Ar matrix from nearly free rotation to perturbed rotation and then to a pendular state bound in the Stark potential well. The perturbed rotation of HCl is characterized by the appearance of the vibrational band center peak and is observed even at mild field strength (\(>1 \times 10^7\) V\(\cdot\)m\(^{-1}\)). The pendular state of HCl appears at the field strength above \(\sim 6 \times 10^7\) V\(\cdot\)m\(^{-1}\), which is indicated by the disappearance of the R(0) peak and the narrowing of the band center peak. Further increase in the field strength increases the degree of dipole alignment along the field direction, approaching an asymptotically perfect orientation (\(<30^\circ\) ), which is indicated by a linear frequency shift with the field strength. To the best of our knowledge, this is the first observation of a field-induced transition of a free rotor to a harmonically bound pendular state in a solid matrix and also the highest degree of field orientation of a diatomic molecule achieved in a static electric field. We expect that the present method will be applicable to the orientation of a wide variety of small polar molecules in low-temperature matrices for the study of spectroscopy and dynamics of oriented molecules.

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NOTES
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