Brute Force Orientation of Matrix-Isolated Molecules: Reversible Reorientation of Formaldehyde in an Argon Matrix toward Perfect Alignment

Youngwook Park, Hani Kang, and Heon Kang*

Abstract: Brute force orientation by an electric field is a promising way of controlling the orientation of polar molecules in the gas phase, but its application to condensed-phase molecules has been very limited. We studied the reorientation of formaldehyde molecules in a solid Ar matrix under the influence of a strong electric field using reflection absorption infrared spectroscopy. Asymptotically perfect alignment of the formaldehyde molecules along the field was achieved at field strengths exceeding $1 \times 10^6 \text{ Vm}^{-1}$. The vibrational bands of the aligned molecules exhibited a unidirectional Stark shift proportional to the field strength. The reorientation of the molecules was reversible despite the cryogenic solid environment of the system.

Manipulation of the spatial orientation of molecules is one of the most important and intriguing subjects in molecular science and engineering. Control of the molecular orientation is especially important for molecular spectroscopic studies and for evaluation of the steric effect in chemical reaction dynamics.[3] Brute force orientation, which makes use of the electrostatic interaction between the permanent dipole moment of molecules and a uniform external electric field, has been widely employed to orient polar molecules in the gas phase because of its simplicity in terms of principle and experimental setup.[2] When the interaction energy exceeds the rotational energy of the free molecules, the rotational motion changes into hindered or pendular motion and the molecules are preferentially oriented along the direction of the electric field. The net orientation achieved by this method, however, is rather small because of limitations in the strength of the applied field. The degree of orientational polarization is remarkably increased by trapping molecules in superfluid He droplets at a very low temperature (about 0.4 K).[2d] For liquids at room temperature, the net polarization is so small at field strengths below the threshold of dielectric breakdown that the associated spectral changes can only be detected by using a phase-sensitive detection method coupled with an applied AC field.[2e]

Despite considerable progress in the utility of brute force orientation, this method has not yet been successfully applied to controlling the direction of condensed-phase molecules. A major hurdle impeding the progress in this research direction is the application of an electric field stronger than the local field of the molecule-solvent interaction to facilitate molecular reorientation. Recently, Shin et al.[3] developed an ice film nanocapacitor method for the application of an electric field of up to $4 \times 10^6 \text{ Vm}^{-1}$ to frozen molecular films inside a vacuum chamber. In the present work, we use this device to reorient formaldehyde (CH$_3$O) molecules in an Ar matrix with an external field. Reversible reorientation of CH$_3$O molecules from isotropic orientation at zero field toward asymptotically perfect alignment at fields stronger than $1 \times 10^6 \text{ Vm}^{-1}$ is demonstrated.

An ice film nanocapacitor sample was prepared as shown in the inset of Figure 1 in order to study the reorientation of CH$_3$O molecules under the influence of an applied field. First, an amorphous D$_2$O film (25 ML thickness; ML = monolayer; 1 ML = $1.1 \times 10^{15}$ molecules cm$^{-2}$) was laid on a Pt(111) substrate at low temperature (about 7 K). On top of the D$_2$O film, an Ar film (240–480 ML) containing CH$_3$O molecules was sandwiched between two Ar spacer layers (48 ML each). Finally, the sample was capped with an amorphous D$_2$O film.

A positive charge layer was formed by soft-landing Cs$^+$ ions on the D$_2$O film surface.[3,4] An equivalent amount of negative charge was induced on the metal substrate surface, thereby forming a parallel plate capacitor. The thickness of the whole sample was 160–300 nm.

Figure 1. RAIR spectra of CH$_3$O trapped in Ar matrix. a) Absorbance spectrum at zero field. CH$_3$O monomer peaks are labeled ($v_1$, $v_2$, $v_3$, $v_4$, $v_5$, $v_6$, $v_7$, and $v_8$). The peaks of CH$_3$O dimer and clusters appear near the monomer peaks. Baseline tilting due to multiple reflections in the film was corrected numerically. b) Difference absorbance of the sample measured at applied field of $5 \times 10^6 \text{ Vm}^{-1}$ and at zero field, showing prominent increase of three ($v_4$, $v_6$, and $v_7$) peaks of CH$_3$O monomer under the field. The inset shows the sample structure.
Figure 1a shows the spectrum of the CH₂O molecules trapped in an Ar film measured by reflection absorption infrared spectroscopy (RAIRS) in the absence of an externally applied electric field. The spectrum indicated the presence of CH₂O monomers as well as CH₂O dimers and higher-order multimers in the sample based on comparison with the spectra of CH₂O in an Ar matrix presented in previous studies. The monomer-to-multimer population ratio in the sample was controlled by changing the ratio of the dosing gas (CH₂O and Ar) pressures. If necessary, the population of CH₂O multimers was removed from the sample by decreasing the ratio of the mole fraction of CH₂O to Ar in the samples to below 1:1000.

When an external electric field was applied across the sample by soft-landing Cs⁺ ions on the sample surface, the absorbance of the three bands (symmetric C–H stretch [ν₁, 2798.0 cm⁻¹], C=O stretch [ν₂, 1742.2 cm⁻¹], and CH₂ bend [ν₃, 1499.1 cm⁻¹]) of CH₂O monomer increased noticeably (Figure 1b). The corresponding multimer bands did not exhibit a noticeable increase. Accordingly, the monomer bands in the difference spectrum appeared very sharp. The transition dipole moments of the three bands are parallel to the permanent dipole moment of the CH₂O molecule. Because the incident IR beam was p-polarized and the field was applied along this direction (which is defined as the Z-axis, normal to the metal surface), the simultaneous increase of these bands indicated alignment of the CH₂O dipole along the field direction. In addition to the use of p-polarized light, the RAIRS selection rule for surface species promoted preferential detection of the field-oriented (surface normal) CH₂O molecules.

Figure 2a displays the field-induced changes of the most intense band, that is, the C=O stretch, with an increase in the field strength. The spectral changes were characterized by two features: an increase of the absorbance and a red-shift of the band position. As mentioned above, the increase in the absorbance resulted from field-induced alignment of CH₂O. Since the absorbance is proportional to cos²θ, where θ is the angle between the p-polarization of the IR beam and the light-absorbing oscillator, and the applied field is along the polarization direction, the ratio of the absorbances with and without the field, A/A₀, is a measure of the orientational polarization of the molecules. Figure 2a shows that the A/A₀ ratio increased with increasing field strength. At field strengths above 1.2 × 10⁸ V m⁻¹, the absorbance did not show a further significant increase, implying asymptotic alignment of the CH₂O molecules.

The red-shift of the band at high fields resulted from a vibrational Stark shift of the field-aligned molecules. The unidirectional frequency shift provides additional evidence that the molecules are aligned along the field. For an ensemble of randomly oriented molecules, the vibrational Stark effect results in a broadening of the band rather than a shift of the band position. The initial increase of the absorbance of the band followed by the frequency shift at higher field strength can be explained as follows. At moderate field strength (of the order of 10⁸ V m⁻¹), molecular reorientation occurs with a certain degree of accompanying vibrational Stark shift, as shown in the difference spectrum (red dashed line in Figure 2a). When the field strength exceeds 1 × 10⁹ V m⁻¹, the region approaching full dipole alignment, the difference spectrum mainly shows a unidirectional frequency shift, with an insignificant increase of the absorbance (blue dashed line in Figure 2a).

The spectra in Figure 2b were obtained while decreasing the applied field; this was achieved by spraying low energy electrons onto the sample surface. When the field strength was reduced, the peak position shifted backward (blue-shift) and the absorbance decreased. These results indicate that the spectra changed reversibly with applied field strength.

The change of the molecular orientation with applied field was analyzed using a thermodynamic model. In this model, the orientational distribution of the CH₂O molecules is assumed to follow Boltzmann distribution with dipolar potential energy, U = −μFcosθ, where μ is the permanent dipole moment of CH₂O, F is the electric field strength, and θ is the angle between the dipole moment and the electric field directions. If the transition dipole moment of a vibration is parallel to the permanent dipole moment of the molecule, then the absorbance of the vibrational band is expressed by Equation (1),

\[ A = \frac{\int_0^\beta \cos^2\theta e^{-\mu F \cos\theta \sin\theta} d\theta}{\int_0^\beta e^{-\mu F \cos\theta \sin\theta} d\theta} = 1 - \frac{2}{\beta} \left( \coth\beta - \frac{1}{\beta} \right) \]  

where β = μF/k_BT; T is the sample temperature and k_B is the Boltzmann constant. For isotropic molecules at zero field, the absorbance is given by: A₀ = 1/3. Therefore, the relative absorbance at a given value of β is expressed by Equation (2).
is determined with its value at 1 \( V_m \) at 7K, \( V_m = 56 \). The plots in the Figure S2 gives the Stark tuning value was calculated by integrating the band intensities. Ther rotational motion may be \( \beta = \frac{\theta}{\alpha} \) is also marked on the right ordinate. The population ratio \( c_1 \) of CH\(_2\)O to \( Ar \) in the sample was about 1:1000.

\[
\frac{A}{A_0} = 3 - \frac{5}{\beta} \left( \coth \beta - \frac{1}{\beta} \right) \tag{2}
\]

Figure 3 shows a plot of the experimentally measured \( A/A_0 \) value for the C=O stretching band as a function of \( \beta \). The data points from ten separate experiments are shown overlapped. Theoretical model (see the text) is presented as black solid line. The (cos\( \theta \)) value is indicated on the right ordinate. The population ratio of CH\(_2\)O to Ar in the sample was about 1:1000.

\[
A/A_0 = \frac{1}{1-fa2 \frac{3e}{4a2 + 1} F_m} \tag{3}
\]

where \( f \) is the reaction field factor, \( \alpha \) is the polarizability of CH\(_2\)O, and \( \epsilon \) is the relative permittivity of the surrounding matter (see section A in the Supporting Information for the derivation and calculation). The plots in Figure 3 are expressed with respect to the local field strength.

The experimental data points closely follow the virtual line (gray dashed line), which was obtained by rescaling the theoretical \( A/A_0 \) value by a factor of 1.07. Apart from this adjustment of the absorbance scale, the field-dependent changes of the experimental and theoretical \( A/A_0 \) curves agree, which clearly supports the proposal that the dipolar orientation of CH\(_2\)O undergoes equilibration based on the applied field strength. It also shows that the net molecular orientation at higher field approaches perfect alignment. The discrepancy between the experimental and theoretical \( A/A_0 \) values of about 7\% cannot yet be clearly explained. We speculate that if the initial orientation of CH\(_2\)O molecules in the thin film was anisotropic with preference for surface-parallel adsorption geometry (\( A_0 < 1/3 \)), then the observed positive deviation of the experimental data could be explained. Inaccurate estimation of the local field could also contribute to the discrepancy. However, adjusting the local field scale alone could not provide a match of the experimental and theoretical curves.

The reversibility of the field-dependent reorientation indicates that trapped CH\(_2\)O molecules rotate quite easily inside the matrix. However, the molecules are not free rotors, as inferred from the absence of rotational structures in the IR spectrum at zero field.[24] The rotational motion may be hindered inside the matrix. For the occurrence of hindered rotation, the rotational energy barrier must not be too large compared to the thermal energy (roughly 60 J mol\(^{-1}\) at 7 K), and at the same time, must be smaller than the electrostatic reorientation energy of the dipole (roughly 500 J mol\(^{-1}\) at 1 \( \times \) \( 10^6 \) V m\(^{-1}\)). If we consider that the molecular size of CH\(_2\)O (diameter = roughly 2.6 Å) is smaller than the size of a single-substitutional site in the Ar matrix (spherical cavity diameter = 3.76 Å),[13] it seems reasonable to assume that a CH\(_2\)O molecule sitting inside a vacant cavity of the matrix undergoes hindered rotation. We have applied this method to other molecules and observed successful alignment of small molecules like HCl and H\(_2\)O, but not a larger one like acetone.

The field-dependent behaviors of the two other bands (symmetric C–H stretch and CH bend) were similar to that of the C=O stretching band, where the absorbance of the band increased and the peak position shifted with the applied field (see section B in the Supporting Information). Interestingly, however, two bands showed a blue shift with applied field (Figure S1), which is opposite to the direction of the C=O band shift. These opposite changes can be understood in terms of the difference in the directions of the transition dipole moments of these vibrational modes with respect to the molecular permanent dipole. The extent of the frequency shift (red or blue) of the three bands was proportional to the applied field strength in the strong molecular alignment regime (> 1 \( \times \) \( 10^6 \) V m\(^{-1}\)), as shown in Figure S2. The slope of the \( \Delta \nu \) versus \( F \) plots in the Figure S2 gives the Stark tuning rate of the vibrational bands: \( \Delta \nu(C=O \text{~stretch}) = -1.1 \pm 0.1 \text{~cm}^{-1}/(10^6 \text{~V~m}^{-1}) \), \( \Delta \nu(\text{symmetric C–H~stretch}) = +2.7 \pm 0.4 \text{~cm}^{-1}/(10^6 \text{~V~m}^{-1}) \), and \( \Delta \nu(CH_3\text{~bend}) = +0.60 \pm 0.08 \text{~cm}^{-1}/(10^6 \text{~V~m}^{-1}) \). Note that \( \Delta \nu \) is determined with its sign included for the aligned molecules, whereas only an absolute \( \Delta \nu \) value can be obtained from the Stark effect (band broadening) of randomly oriented molecules.[9]

In summary, the field-dependent absorbance change of the vibrational bands of CH\(_2\)O and the unidirectional Stark shift of these bands at high field clearly show that the orientation of CH\(_2\)O molecules in the Ar matrix is in dipolar equilibrium with the applied field, leading to asymptotically perfect alignment of the molecules at fields stronger than 1 \( \times \) \( 10^6 \) V m\(^{-1}\). To the best of our knowledge, this is the first
example of orientation of small polar molecules close to full alignment by electric field in the condensed phase, apart from previous experiments using superfluid He droplets at an applied field strength of the order of $10^6$ V m$^{-1}$.[1,4,2] This method of molecular alignment in matrix-isolated systems may serve as a new platform for condensed-phase molecular spectroscopic studies, as demonstrated by the determination of the Stark coefficient and its sign for CH$_2$O molecules, and may have application in many branches of chemical research with oriented molecules.

**Experimental Section**

The experiments were conducted in an ultra-high vacuum (UHV) chamber equipped with a Fourier-transform infrared (FT-IR) spectrometer, a quadrupole mass spectrometer, a Kelvin probe for film voltage measurements, and a low-energy Cs$^+$ ion gun. Detailed description of the apparatus can be found elsewhere.[10]

The experimental film was prepared on a cold Pt(111) surface (about 7 K) by sequential deposition of the corresponding gases, which were dosed through leak valves into the UHV chamber. D$_2$O (Aldrich, 99 atom% D) was purified by freeze-and-pump-thaw cycles. Ar gas was used from a commercially available Ar gas cylinder. CH$_2$O gas was prepared by thermal decomposition of paraformaldehyde (Alfa Aesar, 97%).[3,5] To isolate CH$_2$O molecules in the solid Ar matrix, Ar and CH$_2$O gases in a predetermined ratio were co-deposited.

The thickness of the film was determined by acquiring a temperature-programmed desorption (TPD) spectrum. The thickness of the D$_2$O film was estimated by comparing the TPD peak area of the film with that of a water monolayer on Pt(111) (thickness of 1 ML of amorphous water at 7 K $= 5.5$ Å).[10] The thickness of the Ar film was estimated by comparing the TPD peak areas for the Ar and D$_2$O signals. The number density of solid Ar was taken from the literature.[10]

A static DC electric field was applied across the film by using the ice film nanocapacitor method, which was described in detail previously.[10] The field strength was increased by the deposition of Cs$^+$ ions on the D$_2$O film surface, whereas the field strength was decreased by exposing the Cs$^+$-deposited film to low energy (roughly 5-eV) electrons.[10] The external field strength applied to the Ar matrix region was estimated from the film voltage by considering the division of the voltage between the Ar and D$_2$O layers [Eq. (4)].

$$ F_0 = \frac{V_{\text{film}}}{d_{\text{Ar}} + d_{\text{D}_2\text{O}}} $$  

where $V_{\text{film}}$ is the voltage across the film measured with a Kelvin probe, and $d_{\text{Ar}}$ and $d_{\text{D}_2\text{O}}$ are the thickness of the Ar and D$_2$O layers, respectively. The relative permittivity of each dielectric layer is $\varepsilon = 1.6$ for $\varepsilon_{\text{D}_2\text{O}} = 2.0$.[17]

RAIRS measurements were conducted using a FT-IR spectrometer with a liquid nitrogen-cooled mercury-cadmium-telluride detector in glancing angle reflection geometry (84°). An incident IR beam was p-polarized by a wire grid polarizer. The IR beam path outside the UHV chamber was purged with dry nitrogen gas. All RAIRS spectra were averaged 256 times with a spectral resolution of 0.5 cm$^{-1}$.

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