

LETTERS

Preferential Stabilization of Different Isomers of Weakly Bound Complexes

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The experimental results reported here demonstrate that weakly bound van der Waals complexes are not necessarily kinetically trapped in different isomeric forms in a supersonic expansion. We have recorded the laser-induced fluorescence spectra of the near T-shaped and linear $\text{He}\cdots\text{ICl}(X\ ^1\Sigma^+, v'' = 0)$ complexes in the $\text{ICl B-X}, 3-0$ spectral region at varying distances along the expansion direction to monitor the populations of the two isomers as the local density, collision frequency, and temperature change. The ratio of the T-shaped to linear complex populations monotonically decreases with increasing downstream distances and thus lower $\text{ICl}(X)$ rotational temperatures. Conversion from T-shaped to linear complexes is still observed at the furthest distances where a temperature of 0.57(8) K is measured.

Introduction

The ability to stabilize weakly bound van der Waals complexes and clusters in supersonic expansions has offered a convenient venue for studying long-range intermolecular forces,¹⁻³ energy transfer mechanisms,^{1,4,5} microsolvation processes,^{6,7} and even bimolecular reaction dynamics.⁸⁻¹⁰ A limitation in using complexes for investigating intermolecular dynamics results if only specific intermolecular geometries are stabilized or accessed. Although a number of spectroscopic studies have detected different stereoisomers of van der Waals complexes comprised of molecules with varying sizes in supersonic expansions,^{5,11-16} the mechanisms and propensities for forming the different isomers and how the relative populations of the isomers may change within the expansion remain uncertain. The experimental results presented here show that conversion between different stereoisomers of van der Waals complexes can occur in a supersonic expansion even under conditions where temperatures are below 1 K.

A typical supersonic expansion is established using a high-pressure gas reservoir comprised of a small concentration of

the molecule of interest entrained in a monatomic carrier gas and a small orifice that allows escape of the gas to vacuum. The hydrodynamic flow through the orifice converts the random motion in the high-pressure region behind the orifice to a directed mass flow in the vacuum, resulting in a quick decrease in temperature, collision frequency, and density with distance from the orifice.^{1,17-19} Weakly bound van der Waals complexes are most efficiently stabilized just downstream of the orifice via three-body collisions, where two of the collision partners are stabilized in the complex and the third takes away the excess energy liberated when forming the complex.¹ In this region of the supersonic expansion, the collision frequency is sufficient for three-body collisions to occur while the local temperature is low enough that the collisions do not dissociate existing complexes. The rapid drop in collision frequency and energy with downstream distance has led to the thesis that the state distributions of stereoisomers of van der Waals complexes are dictated by kinetics rather than by thermodynamics.^{1,20} Experimentalists often accept this thesis and, in an attempt to gain signal-to-noise enhancements in spectroscopic and dynamics studies, often interrogate regions in the expansion within only tens of nozzle diameters downstream from the orifice where

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the densities of the complexes are still high but the effects from collisions are thought to be negligible.

The evolution of an expansion from a continuum to a molecular flow without collisions has been shown to be a gradual process,²¹ in conflict with these often accepted assumptions. In addition, at least two phenomena increase the collision frequency above that predicted using the equations based on ideal gas and rigid sphere models^{17,19} and contribute to uncertainties in the expansion properties. They are quantum effects²² arising from the motion of very cold atoms or molecules and velocity slip¹⁷ in expansions of gaseous mixtures. The quantum effects result, in part, from the large zero point energies and the de Broglie wavelengths of the carrier gas atoms as they are cooled to very low temperatures and give rise to a large increase in the effective collision cross section of the carrier gas atoms. A collision cross section $> 200 \text{ \AA}^2$ is expected for helium atoms at the low temperatures achieved in supersonic expansions.²² The mass of each of the atoms or molecules and the partial pressures of the species in an expansion dictate the terminal velocities achieved by the constituents.¹⁷ The difference in the velocities is referred to as a velocity slip, with the heavier species moving more slowly than the lighter species. Collisions between species with dissimilar masses occur, thereby limiting the ultimate temperatures and internal energies of the molecules within the expansion.

It is important to note that the approximation of a collision-free environment may still be valid if the processes under investigation occur on a much shorter time scale than the time interval between collisions.¹⁹ The distances traveled by weakly bound complexes before they are experimentally probed, however, are typically on the order of tens of nozzle diameters and correlate with microsecond time scales and many collisions. The roles that the expansion conditions have on stabilizing and cooling the complexes via collisions with the carrier gas atoms remain uncertain and will most likely depend on the specific system under investigation. Furthermore, if different stereoisomers exist, the effect the collisions may have on the relative populations of each en route to the region where they are probed has yet to be characterized. We recently reported the observation of discrete spectroscopic features in laser-induced fluorescence, LIF, spectra recorded in the ICl B $^3\Pi_{0+}-X \ ^1\Sigma^+$, 2-0, and 3-0 regions that can be attributed to rovibronic transitions from $\text{He}\cdots\text{ICl}(X, v''=0)$ ground state complexes with distinctly different geometries, a near T-shaped complex, and a more strongly bound linear $\text{He}\cdots\text{I}-\text{Cl}$ isomer.²³ Here we present LIF spectra of the $\text{He}\cdots\text{I}^{35,37}\text{Cl}$ complexes recorded in the ICl B-X, 3-0 region at varying distances downstream in the expansion to determine how the relative populations of the two $\text{He}\cdots\text{ICl}(X)$ isomers vary with increasing distance from the nozzle and thus decreasing local density, collision frequency, and temperature.

Experimental Methods

The ground state $\text{He}\cdots\text{ICl}(X, v''=0)$ complexes were stabilized within a pulsed supersonic expansion comprised of iodine monochloride with a concentration of ~ 12 ppm in a helium buffer gas maintained at a total pressure of 140 psi relative to the atmosphere. The pulsed valve with an orifice diameter, d , of $800 \mu\text{m}$ was operated at 10 Hz. The LIF spectra were recorded using a pair of commercial Nd:YAG pumped dye lasers operating with rhodamine 6G dye. The first laser, with a frequency resolution of 0.2 cm^{-1} , was used to record spectra of the $\text{He}\cdots\text{ICl}$ complexes in the ICl B-X, 3-0 region, 17810 to 17860 cm^{-1} . The second laser, with a resolution of 0.06 cm^{-1} , was used to record spectra of the I^{35}Cl B-X, 2-0 rovibronic

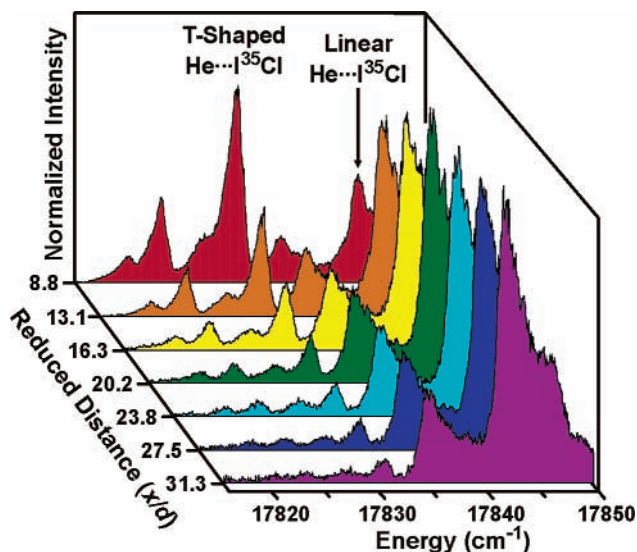


Figure 1. Laser-induced fluorescence spectra of $\text{He}\cdots\text{I}^{35,37}\text{Cl}$ complexes recorded in the ICl B-X, 3-0 spectral region at varying reduced distances x/d , where x is the distance downstream from the nozzle and d is the diameter of the nozzle orifice, $800 \mu\text{m}$. The intensities of features associated with transitions of the T-shaped and linear $\text{He}\cdots\text{I}^{35}\text{Cl}(X)$ isomers at 17831 and 17842 cm^{-1} , respectively, track the change in the populations of the ground state isomers as a function of x/d .

band with rotational line resolution. The laser pulse energies were measured to be ~ 30 and $\sim 7 \text{ mJ/pulse}$, respectively, within the vacuum chamber. A 1 m focal length lens was used to focus the laser beams to a diameter of $\sim 3 \text{ mm}$ at the same position in the supersonic expansion region. Resultant fluorescence was collected with a telescope assembly and imaged onto a visible wavelength photomultiplier tube. A boxcar integrator was used to record the intensity of the LIF as a function of laser frequency. An LIF spectrum of the $\text{He}\cdots\text{ICl}$ complexes in the 3-0 region was first recorded at a given distance downstream from the pulsed valve, x . An LIF spectrum of the I^{35}Cl 2-0 band was then recorded to determine the $\text{I}^{35}\text{Cl}(X, v''=0)$ Boltzmann rotational temperature at this position in the expansion. Spectra were recorded with the lasers intersecting the expansion at seven different distances from the pulsed valve orifice, $x = 7, 10.5, 13, 16, 19, 22,$ and 25 mm .

Results

The LIF spectra recorded in the ICl B-X, 3-0 region are plotted in Figure 1 as a function of transition energy and reduced distance, x/d . A weak structureless continuum signal is subtracted from each of the spectra, and the spectra are normalized to the same integrated fluorescence intensity. The fluorescence excitation features that can be observed in the 3-0 region are most easily recognized in the spectrum recorded at $x/d = 8.8$. The features at 17820 and 17828 cm^{-1} are attributed to the I^{37}Cl and I^{35}Cl B-X, 3-0 monomer bands. These transitions access rotational levels that are very short-lived, $\sim 200 \text{ ps}$, due to a curve crossing of the ICl B state by a repulsive Z1 state near the ICl(B, $v'=3$) region,^{24,25} and as a result very weak fluorescence signals are observed. The bands at 17824 and 17831 cm^{-1} are attributed to transitions from the first excited intermolecular level in the $\text{He} + \text{I}^{37}\text{Cl}(X, v''=0)$ and $\text{He} + \text{I}^{35}\text{Cl}(X, v''=0)$ ground states with near T-shaped geometries to the lowest energy level within the $\text{He} + \text{I}^{37}\text{Cl}(B, v'=3)$ and $\text{He} + \text{I}^{35}\text{Cl}(B, v'=3)$ excited states also with a near T-shaped orientation.^{23,26} The two higher energy bands at 17835 and 17842

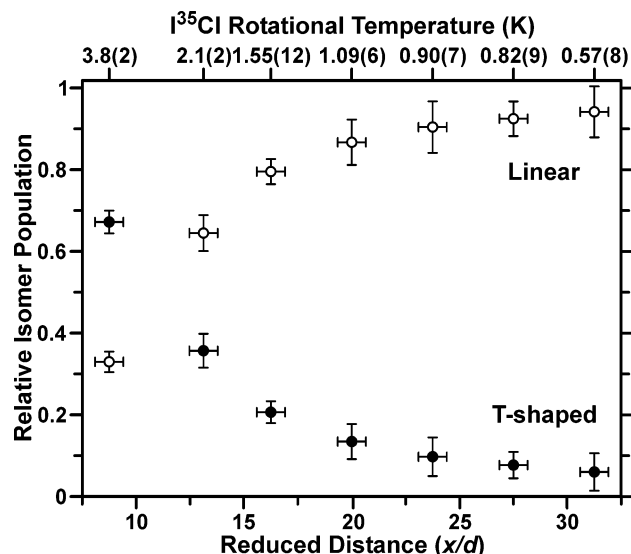


Figure 2. Relative peak intensities of the T-shaped and linear $\text{He}\cdots\text{I}^{35}\text{Cl}$ fluorescence excitation features at 17 831 and 17 842 cm^{-1} , respectively, plotted as a function of reduced distance along the expansion. The $\text{I}^{35}\text{Cl}(X, v''=0)$ rotational temperature determined at each distance is shown on the top abscissa.

cm^{-1} have been assigned to transitions of the $\text{He}\cdots\text{I}^{37}\text{Cl}$ and $\text{He}\cdots\text{I}^{35}\text{Cl}$ complexes from the lowest energy intermolecular level of the ground state with a linear equilibrium geometry to the second excited intermolecular vibrational level within the electronically excited state, respectively.²³ The $\text{He}\cdots\text{I}^{35,37}\text{Cl}(B, v'=3)$ excited state complexes undergo vibrational predissociation, forming separate $\text{He} + \text{I}^{35,37}\text{Cl}(B, v'=2)$ fragments on a time scale that is comparable to that for $\text{I}^{35,37}\text{Cl}(B, v'=3) \rightarrow \text{I}^2\text{P}_{3/2} + \text{Cl}(^2\text{P}_{3/2})$ dissociation.^{23,26,27} The $\text{I}^{35,37}\text{Cl}(B, v'=2)$ products are long-lived, $\sim 6 \mu\text{s}$, and relax via fluorescence, which is in turn detected in LIF spectroscopy experiments.

The population of each $\text{He}\cdots\text{I}^{35}\text{Cl}(X, v''=0)$ ground state isomer as a function of x/d could, in principle, be tracked by measuring the integrated intensity of the 17 831 and 17 842 cm^{-1} features. The integrated intensity of a $\text{He}\cdots\text{ICl}$ fluorescence feature is proportional to the product of the population of the ground state isomer sampled by the transition, the transition strength for that vibronic band, and the fluorescence quantum yields of the excited state complex and the vibrational predissociation products.²⁸ The spectral overlap of neighboring features in the LIF spectra limits the accuracy with which the integrated intensities of the $\text{He}\cdots\text{ICl}$ bands can be measured. Furthermore, the transition strengths for vibronic transitions of these complexes are not known. We have therefore chosen to monitor the change in the relative populations of the $\text{He}\cdots\text{I}^{35}\text{Cl}(X)$ isomers rather than the actual populations as a function of x/d by measuring the peak intensities of the $\text{He}\cdots\text{I}^{35}\text{Cl}$ bands in the spectra.

The relative intensities of the T-shaped and linear $\text{He}\cdots\text{I}^{35}\text{Cl}$ features, Figure 2, have a strong dependence on reduced distance, x/d . The intensity of the T-shaped $\text{He}\cdots\text{I}^{35}\text{Cl}$ LIF feature is more than twice that of the linear $\text{He}\cdots\text{I}^{35}\text{Cl}$ feature at the smallest reduced distance, $x/d = 8.8$, where an I^{35}Cl rotational temperature of 3.8(2) K was measured. The intensity of the linear feature increases monotonically relative to that of the T-shaped feature with increasing x/d . The linear $\text{He}\cdots\text{I}^{35}\text{Cl}$ feature becomes an order of magnitude more intense than the T-shaped feature at $x/d = 31.3$, for which a rotational temperature of 0.57(8) K was measured. This drastic shift in intensity from the T-shaped to the linear $\text{He}\cdots\text{I}^{35}\text{Cl}$ feature corre-

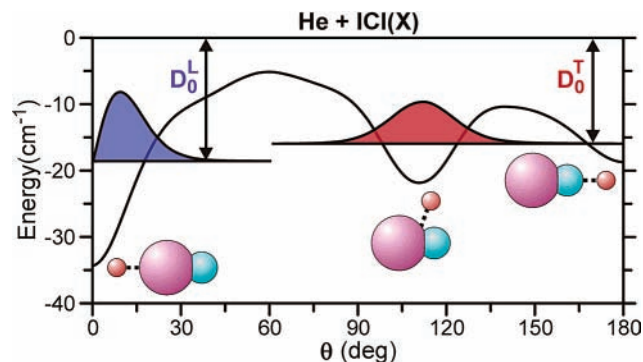


Figure 3. $\text{He}\cdots\text{I}^{35}\text{Cl}(X, v''=0)$ intermolecular adiabatic potential energy calculated as a function of ICl orientation³³ using the ab initio surface of Prosmi et al.³² The probability densities for the two lowest $\text{He}\cdots\text{I}^{35}\text{Cl}(X)$ intermolecular vibrational levels, with binding energies $D_0^L = 18.29$ and $D_0^T = 15.15 \text{ cm}^{-1}$,³² are localized on different regions of the He intermolecular potential energy surface, indicating the existence of at least two distinct isomers.

sponds to a factor of 20 change in the relative populations of the $\text{He}\cdots\text{I}^{35}\text{Cl}(X)$ isomers.

Discussion and Conclusions

While the concept of stereoisomers is commonly accepted for molecules, a corresponding definition at the quantum mechanical level has not yet been formalized.^{29,30} A qualitative description of stereoisomers is often associated with a compound comprised of molecules that have the same number, kind, and connectivity of atoms, but differ in their spatial orientation. The quantum mechanical interpretation of this definition is that the potential energy surface characterizing a compound has multiple minima located at different structural orientations. If the wave function of the compound in a specific quantum state is localized in a minimum with negligible amplitude outside of that region and if another state is localized in a different minimum, then the compound is said to have at least two stereoisomers.²⁹ The concept of stereoisomers of van der Waals complexes is even harder to accept, since the interactions are dominated by long-range electrostatic forces and, as a result, the moieties are often weakly bound. Consequently, van der Waals complexes are regularly found to be floppy with wave functions spanning wide regions of the potential energy surface, sampling varying intermolecular geometries and structures.

Ab initio calculations of the $\text{He} + \text{I}^{35}\text{Cl}(X \ ^1\Sigma^+, v''=0)$ ground state interactions indicate minima in the ground state potential energy surface at the linear $\text{He}\cdots\text{ICl}$, near T-shaped, and antilinear $\text{He}\cdots\text{CII}$ orientations.³¹ The two lowest $\text{He}\cdots\text{ICl}(X, v''=0)$ intermolecular vibrational states are predicted to be bound by 18.29 and 15.15 cm^{-1} while the potential has a global minimum in the linear orientation with a depth of 58.62 cm^{-1} . Recent experiments have determined that the binding energy of the lowest ground-state intermolecular level with a linear equilibrium geometry is 22.3(1.2) cm^{-1} ,³² in remarkable agreement with these predictions. An adiabatic potential surface for the $\text{He}\cdots\text{ICl}(X, v''=0)$ complex was calculated as a function of the ICl orientation³³ using the ab initio surface,³¹ Figure 3. The probability densities for the two lowest $\text{He}\cdots\text{ICl}(X, v''=0)$ states are superimposed on the adiabatic potential in Figure 3. The degree of localization of these states indicates that the complexes are localized within the linear and near T-shaped regions of the potential. The significant effective barrier between the linear and near T-shaped orientations, the narrow regions over which the probability densities span, and the lack of nodes in the densities along the angular and He to ICl radial

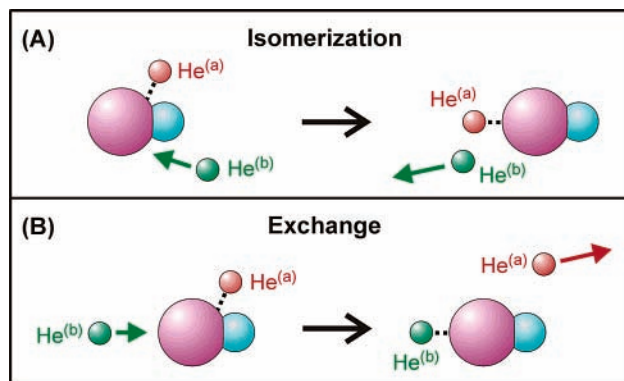


Figure 4. Transfer of population from the T-shaped isomer to the lowest energy, linear isomer may occur via two reaction mechanisms, isomerization and exchange,³⁴ even at the very low temperatures, <2 K, observed in the expansion at $x/d > 10$.

coordinates all suggest that these two states can indeed be considered stereoisomers of the $\text{He}\cdots\text{ICl}$ complex, a near T-shaped isomer and an energetically favored linear $\text{He}\cdots\text{ICl(X)}$ isomer.

The conversion of T-shaped $\text{He}\cdots\text{ICl(X}, \nu''=0)$ complexes into the linear isomer with increasing distance downstream, Figure 2, cannot be attributed to simple cooling of $\text{He}\cdots\text{ICl}$ intermolecular vibrational levels, since these two states represent two distinct stereoisomers of the complex. Simulations of the stabilization of the T-shaped and linear isomers of $\text{Ar}\cdots\text{I}_2(\text{X})$ complexes³⁴ offer insights into two mechanisms by which collisions with He atoms may convert the T-shaped $\text{He}\cdots\text{ICl(X}, \nu''=0)$ complexes into linear isomers even at the very low temperatures observed in our experiments. The first mechanism is that of a conventional isomerization reaction shown in Figure 4, panel A.³⁴ A $\text{He}^{(a)}\cdots\text{ICl(X)}$ complex collides with a second helium atom, $\text{He}^{(b)}$. The colliding $\text{He}^{(b)}$ atom gains kinetic energy during the collision because of the attraction associated with the $\text{He}^{(b)}\cdots\text{He}^{(a)}\cdots\text{ICl}$, atom-complex van der Waals potential. This kinetic energy results in an increase in the internal energy of the initial complex perhaps above the barrier along the angular coordinate so that the $\text{He}^{(a)}$ atom can transfer from one well into the other. The $\text{He}^{(b)}$ atom then takes away the excess energy as the complex relaxes in the other isomeric form. The second mechanism is that of an exchange reaction or swap mechanism, Figure 4, panel B.³⁴ The colliding $\text{He}^{(b)}$ atom approaches an unoccupied well of the complex, forming a metastable $\text{He}^{(b)}\cdots\text{He}^{(a)}\cdots\text{ICl}$ collision complex. The internal energy of the collision complex may be greater than the $\text{He}^{(a)} + \text{ICl}$ binding energy and the dissociation of the $\text{He}^{(a)}$ atom would result. Theoretical simulations of the cooling of the $\text{He}\cdots\text{ICl}$ isomers, performed in a manner similar to those of $\text{Ar}\cdots\text{I}_2$,³⁴ would provide additional scrutiny of these mechanisms and of the details of the ground state potential energy surface.

While the dominant mechanism for conversion of T-shaped $\text{He}\cdots\text{ICl(X)}$ complexes to the energetically favored linear $\text{He}\cdots\text{ICl(X)}$ isomer has not been precisely determined, it is clear that the complexes are not kinetically trapped in the different potential minima. These results offer additional promise for using van der Waals complexes in investigations of intermolecular interactions and dynamics, since complexes with different

orientations can be preferentially stabilized by changing the distance and temperature region within the expansion that is probed. At the same time, it may also be useful to record spectra of van der Waals complexes at multiple distances downstream, and thus in varying local density, collision frequency, and temperature regimes within the expansion, to identify features that can be attributed to transitions of different stereoisomers.

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