0.90 eV. Physically we envision the captured electron staying in the resonance state for only a fraction of the vibrational cycle, and during this short time the modified electronic distribution gives an impulse to the nuclei, which begin to move. A greater impulse to the Cl nucleus occurs when the Cl has greater added electronic charge; this occurs in the (approximately) symmetric $\pi_m$ molecular orbital (approximately symmetric because the thermally distorted molecule has, strictly speaking, only unit symmetry; the $\Sigma-\Pi$ coupling arguments of Clarke and Coulson$^7$ are valid for the ideal geometrical configuration but are relaxed by certain out-of-plane vibrations). Accordingly, we identify the lowest resonance in the electron transmission study of C$_5$H$_7$Cl which occurs close to the peak of the dissociative attachment resonance as being due to electron capture into a symmetric $\pi_4$ state. For C$_6$H$_4$F, by analogy, we prefer the same assignment.


Comment on the role of constraints on the conformational structure of n-butane in liquid solvents

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There are now a number of published computer simulations of the dynamics of flexible chain molecules in condensed phases. Some of these describe true Newtonian trajectories,$^1$ and others discuss stochastic trajectories$^7$ (e.g., Brownian dynamics) in which the effects of the solvent surrounding the chain molecule are modeled with stochastic elements. The phenomena investigated in these studies focus on the conformational structures and rates of conformational transitions in the chain molecules. For example, in a n-butane molecule, the principal internal degree of freedom is the dihedral angle, $\phi$, and one is interested in the effects of the condensed phase on the distribution function for that angle, $s(\phi)$, and on the rates between the stable trans (\phi near 0) gauche (\phi near ±2\pi/3) states.

There are other internal degrees of freedom too. But these are less important because so-called "hard" intramolecular forces nearly constrain those coordinates to particular points in configuration space. For example, in n-butane, which can be modeled as four extended atoms (representing two CH$_3$ groups and two CH$_2$ groups), the bond lengths between adjacent carbons fluctuate very little from 1.53 Å, and the angles between adjacent C–C bonds remains close to the tetrahedral angle, 109°. Since these degrees of freedom are relatively unimportant, it seems reasonable that the dynamics of the relevant degrees of freedom can be accurately modeled by assuming that the nearly constrained internal motions are indeed rigid. Then the irrelevant internal degrees of freedom would be eliminated through the introduction of holonomic constraints. This type of procedure can be computationally convenient, especially in light of the SHAKE algorithm$^{11}$ that can be used to perform constrained dynamics. But remarkably, the procedure of replacing the actual hard forces with rigid constraints is not altogether insignificant. In a constrained trajectory, the momenta conjugate to the constrained coordinates are set to zero. However, in an unconstrained trajectory, these momenta are not zero no matter how strong the hard potentials become which tend to fix the configurations of the coordinates. Indeed, at thermal equilibrium, there is a Boltzmann distribution of these momenta. Thus, it is clear that the constrained dynamical trajectories cover a different region of phase space than trajectories performed with hard forces. Thus, the equilibrium averages associated with the two types of trajectories can be different. This fact has frequently been appreciated and commented upon by others in the recent literature.$^{12-15}$ The purpose of this note is to describe the size of the differences for n-butane.

As reviewed by Fixman,$^{12}$ one may compute the differences a priori by determining how the kinetic energy of the constrained dynamical system depends upon configurations. (The kinetic energy of an unconstrained
s(\phi) = c s_{s}(\phi) / \left[ g(\phi) \right]^{1/2},

where c is a normalization constant. It is readily shown that this result is correct whether the \( n \)-butane molecules are isolated in the gas phase or as a solute in a condensed phase at infinite solute dilation. In Ref. 6 we presented a molecular dynamics computation the solvent contribution to \( s_{s}(\phi) \) for carbon tetrachloride solvent. Its logarithm gives the solvent contribution to the potential of mean torsion, \( \Delta w_{s}(\phi) \). If a simulation had been performed with flexible \( n \)-butane, the potential of mean torsion obtained would be \( \Delta w(\phi) = \Delta w_{s}(\phi) + \frac{1}{2} k_{T} \ln g(\phi) + \text{constant} \). These potentials of mean torsion are graphed in Fig. 1 along with the approximate two-cavity theoretical prediction. 14 The theoretical model is based on statistical mechanics which does not artificially couple coordinates to momenta by introducing holonomic constraints. Thus, the approximate model should be compared with \( \Delta w(\phi) \) and not \( \Delta w_{s}(\phi) \).

For this particular system, whether or not the irrelevant degrees of freedom in the \( n \)-butane molecule are taken to be constrained, we find the solvent shift of the \( \text{trans-gauche} \) equilibrium to be \( K/k_{T} \approx 1.5 \). However, the constraints increase the likelihood of molecules in the vicinity \( \text{trans-gauche} \) transition state (\( \phi \) near 1\( \pi \)) by 20% to 30%. Thus, the constraints may be of greatest significance for transition rates in this system.

This note owes its existence to a conversation with Eugene Helfand during which Dr. Helfand alerted us to the fundamental differences in the intramolecular distribution functions for flexible and nonflexible molecules and pointed out the discussions of the differences in Refs. 12–15.

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