

does not exhibit the rainbow structure. The discrepancies at center-of-mass angles $\theta \lesssim 3^\circ$ may be due to experimental uncertainties arising from large corrections to account for a background peaked at $\theta = 0^\circ$. The possibility that this disagreement is due to breakdown of the IOS in the forward direction is not conceivable because very good agreement is obtained for the vibrational inelastic differential cross sections.¹⁵

Final vibrational distributions for the inelastic and the CT processes are shown in Fig. 2. Both theoretical results are presented with their absolute values and the experiments have been normalized to the CTIOSA curves at $v_f = 1$. The agreement between experiment and CTIOSA is very good whereas the TSH results, as well as the frequently postulated Franck-Condon distributions, are seen to deviate significantly.

In conclusion we have shown that a quantum mechanical treatment of both the inelastic and the charge transfer nonadiabatic processes is feasible and provides a superior description of the experiments compared to the TSH treatment. This demonstrates for the first time the importance of

quantum effects in ion-molecule charge transfer.

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Study of the transition state region in the Cl + HCl reaction by photoelectron spectroscopy of ClHCl⁻

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A central goal of reaction dynamics has been to gain a microscopic understanding of chemical bond formation and cleavage during a reactive collision. This requires a knowledge of the potential energy hypersurface for a chemical reaction, especially near the transition state, as this is the region of the surface that determines the outcome of a collision.¹ Our experiments represent a significant departure from the state-to-state chemistry approach to this problem which has been developed over the last ten years.² We probe the transition state region for a neutral reaction not by a collision, but rather by photodetachment of a stable anion geometrically similar to the neutral transition state. Specifically, we have studied the Cl + HCl and Cl + DCl hydrogen exchange reactions by photoelectron spectroscopy of ClHCl⁻ and ClDCl⁻.

The principle behind these experiments is that the photoelectron spectrum of ClHCl⁻ probes the region of the Cl + HCl potential surface which is accessed when the ion is photodetached. Matrix isolation studies³ indicate that the ion is linear and symmetric, and the Cl-Cl equilibrium distance is calculated⁴ to be 3.2 Å. A comparison to *ab initio* calculations⁵ of the Cl + HCl potential energy surface, which predict a linear or nearly linear transition state, indi-

cates that photodetachment should access the transition state region. This reaction is of particular interest since its potential energy surface is predicted to support quasibound ClHCl states in the transition state region.⁶ The observation of features in the photoelectron spectrum of ClHCl⁻ attributable to these states would provide a detailed spectroscopic probe of the reactive surface.

The photoelectron spectrometer used in these studies is similar in principle to that recently described by Posey.⁷ ClHCl⁻ is generated by expanding a mixture of NF₃, HCl, and Ar through a pulsed molecular beam valve and crossing the neutral beam with a 1 keV electron beam just outside the valve orifice. The ions are mass selected with a time-of-flight mass spectrometer. The mass-selected ions are irradiated by an excimer laser pulse, and a small fraction of the ejected photoelectrons is energy analyzed with a second time-of-flight system.

The figure shows the photoelectron kinetic energy spectra for ClHCl⁻ and ClDCl⁻. The spectra were taken using the ArF laser line at 6.42 eV. The energy scale was calibrated from the photoelectron spectra of I⁻, F⁻, and CN⁻. The electron energy resolution at 1.5 eV was 35 meV. Both spectra were averaged for 200 000 laser shots. The background

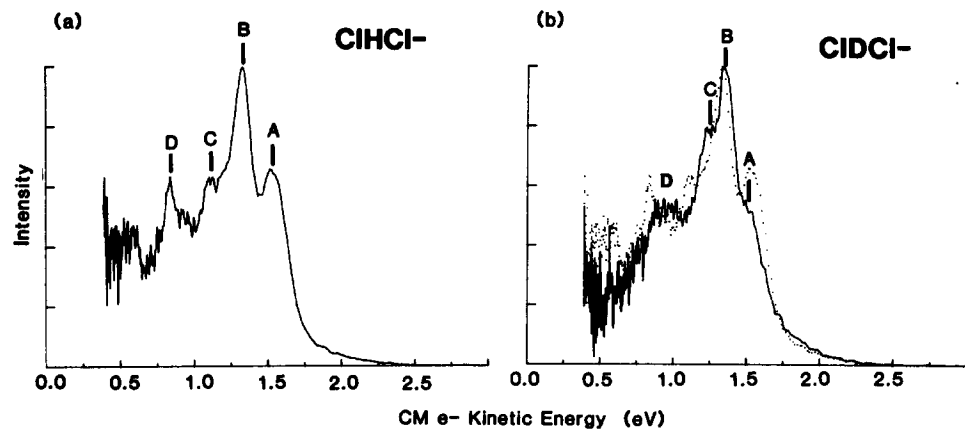


FIG. 1. (a) Photoelectron spectrum of ClHCl⁻. Peak energies: A = 1.524 eV, B = 1.326 eV, C = 1.109 eV, and D = 0.840 eV. Uncertainty in peak positions is 0.010 eV. (b) Superposition of photoelectron spectrum of ClDCl⁻ (solid) and ClHCl⁻ (dots). Peak energies: A = 1.51 eV, B = 1.35 eV, C = 1.24 eV, and D was too broad to assign. Peak positions have an average uncertainty of 0.015 eV.

photoelectron signal generated by stray ArF photons⁸ was subtracted from these spectra.

The best estimates for the centers of the partially resolved peaks in both energy spectra are indicated in Fig. 1. Although it is difficult to assign accurate energies to peaks A and C in the ClDCl⁻ spectrum, the superimposed spectra in Fig. 1(b) show that peak A is at nearly the same energy in both spectra, but the spacing between the peaks in the ClDCl⁻ spectrum is less than in ClHCl⁻. This suggests we are observing a progression in a vibrational mode of the ClHCl complex involving H atom motion, and peak A at 1.524 eV is from the 0-0 transition. The nature of the complex must be that the H atom is interacting strongly with both Cl atoms; if we were accessing the reactant or product valley of the Cl + HCl surface, a considerably higher frequency progression in the HCl stretch (0.357 eV) would be expected. From the electron affinity of Cl (3.617 eV)⁹ and the dissociation energy of ClHCl⁻ (1.02 eV),¹⁰ any structure at electron kinetic energies below 1.78 eV in an ArF photoelectron spectrum corresponds to neutral states that lie above the Cl + HCl ($v = 0$) asymptote. Thus, all the peaks represent transitions to states that can dissociate to Cl + HCl ($v = 0$).

A possible interpretation of these results is suggested by the theoretical study of Bondi⁶ on the collinear Cl + HCl reaction. Their calculation of the reaction probability as a function of reactant collision energy showed sharp resonance structure. This was interpreted in terms of a set of vibrationally adiabatic curves in hyperspherical coordinates that show how the energy of each asymmetric stretch (v_3) state of the ClHCl complex depends on the distance between the two Cl atoms, and, in particular, how the v_3 states evolve into HCl vibrational states in the asymptotic limit. The LEPS surface used in their calculations, which has a 9 kcal/mol barrier, yields repulsive curves for the $v_3 = 0$ and the odd v_3 levels, but the even v_3 curves with $v_3 \geq 2$ have wells which support a small number of symmetric stretch states of the complex. These are long-lived states which can decay to Cl + HCl and are responsible for the reactive resonances¹¹ found in the scattering calculation for this reaction.

A preliminary analysis shows that the peaks in our spectra are in qualitative accord with Bondi's calculation assuming we observe a progression in the asymmetric stretch in the ClHCl complex. Only transitions to even v_3 levels of the

neutral are allowed from the ground vibrational state of the ion. Fitting the experimental peaks to an anharmonic oscillator yields $\omega_e = 0.082 \pm 0.010$ eV and $\omega_e x_e = -0.0044 \pm 0.0015$ eV for ClHCl. The 0-0 transition energy is 4.896 ± 0.005 eV (calculated by subtracting the kinetic energy of peak A from the photon energy). If we calculate the vertical transition energies from the predicted ground state geometry⁴ of ClHCl⁻ to the even v_3 adiabatic curves and fit these results to an anharmonic oscillator, we find $\omega_e = 0.089 \pm 0.016$ eV, $\omega_e x_e = -0.0075 \pm 0.0022$ eV, and the 0-0 transition is 4.768 eV. The addition of zero-point bending energy, which is neglected in the collinear calculation, would raise the energy of the 0-0 transition and result in better agreement with the experiment.

The peaks in our spectrum are considerably broader than the instrumental resolution. This could result either from transitions to repulsive v_3 levels,^{12,13} or from transitions to v_3 levels that support symmetric stretch states which are not resolved in our experiment. For each v_3 , the symmetric stretch states are separated by only 0.03 eV, which is near our resolution limit. In addition, these states can dissociate, and their lifetimes in a real system may be considerably shorter than predicted by a collinear model. Hot band transitions, low-lying electronic states of Cl + HCl,¹⁴ and bending progressions in the ClHCl complex¹⁵ could also contribute to the width of the observed peaks.

In conclusion, our spectra show vibrational structure associated with unbound states of the ClHCl complex which can readily be compared to calculated results on a model surface for the Cl + HCl reaction. Until we resolve the symmetric stretch states, we cannot be certain we are observing long-lived reactive resonance states. Higher resolution experiments are about to begin which should settle this issue.

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NOTES

What is the solvent longitudinal time scale controlling electron transfer rates?

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Solvent motions play a significant role in controlling the rates and the adiabaticity of electron transfer (ET) processes with small activation barriers.¹⁻⁶ As these motions become slow, a nonadiabatic reaction will turn adiabatic. Kosower and Huppert⁶ have found a correlation between photochemical intramolecular ET rates and τ'_1 , the solvent longitudinal time in alcohols. τ'_1 is precisely defined for the Debye model⁷ in which the solvent has a single dielectric relaxation time, τ_1 , i.e., $\tau'_1 = (\epsilon_\infty/\epsilon_0)\tau_1$. Here ϵ_∞ and ϵ_0 denote the optical and the zero frequency values of the solvent dielectric function $\epsilon(\omega)$, respectively. The precise definition of the solvent time scale relevant for ET rates for an arbitrary (non-Debye) solvent is an open question, which is of considerable current interest. Kosower⁶ and Eisenthal⁵ have emphasized the significance of solvent polarity which affects the activation barriers, and whose role should be distinguished from that of solvent dynamics (viscosity).

We have developed a theory for ET rates in polar solvents⁸ by utilizing the formal analogy of this problem with the calculation of nonlinear optical line shapes.^{9,10} The approach is based on reduced equations of motion for the density matrix in Liouville space. An approximate resummation of the perturbative series for the rate to infinite order in the electronic coupling was performed, based on the assumption of separation of time scales between the off-diagonal density matrix elements (the coherences) and the diagonal elements (populations). The resulting expression interpolates continuously between the nonadiabatic and the adiabatic limits of the rate, satisfies the detailed balance condition, reproduces the entire Kramers turnover curve as a function of the solvent longitudinal time scale, provides a microscopic definition for the reaction free energy, and generalizes Marcus free energy relation to the adiabatic regime. In this note we

focus on the adiabatic limit whereby the ET rate from state $|a\rangle$ (donor) to $|b\rangle$ (acceptor) is

$$K = (1/\tau_s) \exp(-q_a^2/2), \quad (1a)$$

where $\tau_s = \tau(q_a) + \tau(q_b)$ is the relevant solvent time scale and where $\tau(q_n)$ is the solvent time scale function controlling the ET rate,

$$\tau(q_n) = \exp(-q_n^2/2) \int_0^\infty dt \left\{ \frac{1}{\sqrt{1-M^2(t)}} \times \exp\left[\frac{q_n^2 M(t)}{1+M(t)} \right] - 1 \right\}, \quad (1b)$$

with

$$q_n = \frac{E - \delta_n}{\sqrt{k_B T |\delta_a - \delta_b|}}, \quad n = a, b, \quad (1c)$$

$$Q(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \exp(-i\omega t) \left[\frac{1}{\epsilon_0} - \frac{1}{\epsilon(\omega)} \right], \quad (2)$$

and $M(t) = Q(t)/Q(0)$. Here E is the reaction exothermicity and δ_a (δ_b) is the average value of the solvation coordinate when the ET system is in the state $|a\rangle$ ($|b\rangle$). $q_a^2/2 = \Delta G_{ab}^*/(k_B T)$ and $q_b^2/2 = \Delta G_{ba}^*/(k_B T)$, where ΔG_{ab}^* (ΔG_{ba}^*) is the activation free energy for the forward (reverse) reaction. As the solvent is varied, δ_n and consequently q_n and the activation barriers will vary primarily with the solvent polarity. Approximate relations between δ_n and polarity measures such as ET(30) may be derived¹¹ in agreement with the relationships proposed by Eisenthal.⁵ The dynamical effects of the solvent affect the rate via $M(t)$, which is the normalized correlation function for the longitudinal polarization of the solvent.^{8,12} In order to explore the