

A comparison between theoretical and experimental state-to-state charge transfer cross sections for H^++H_2 at 20 eV: Evidence for quantum effects

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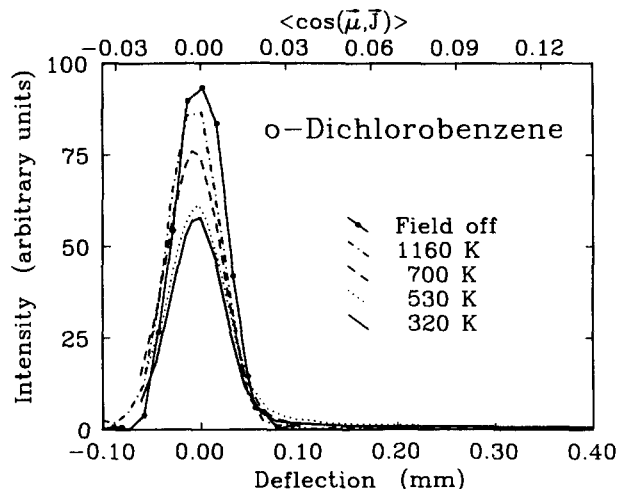


FIG. 2. Deflection distribution of *o*-dichlorobenzene, presented as in Fig. 1. At 1160 K, the field gradient is 50 kV/cm².

cant fraction of the rotational states corresponds to trajectories in which \mathbf{J} precesses about an axis perpendicular to $\boldsymbol{\mu}$, thus averaging the space-fixed dipole to zero. Therefore, even near room temperature, where the density of vibrational states is too low for significant IVRET, the deflection distribution for *o*-dichlorobenzene shown in Fig. 2 has a spike at zero deflection. The magnitude of this peak is similar for 320 and 530 K, as expected for the motion of a rigid rotor. But at higher temperatures, the peak increases until at 1160 K, $\approx 90\%$ of the molecules behave statistically, with deflections less than 1/10th that of rigid rotors. Here the average density of vibrational states is 2×10^9 states/cm⁻¹, and the average vibrational energy is 12 500 cm⁻¹. From Ehrenfest's theorem, the expectation value of the x component of the dipole moment of a particular molecule can be related to the rate of change of the corresponding momentum compo-

nent: $\langle \mu_x \rangle = (dE/dx)^{-1} \langle F_x \rangle = (dE/dx)^{-1} d \langle P_x \rangle / dt$. Thus, for molecules which do not deflect ($\Delta \langle P_x \rangle = 0$) the time average $\overline{\langle \mu_x \rangle}$ of the expectation value of the dipole moment over the beam's 1 ms flight time is zero.

Future publications⁷ will provide a more complete theoretical interpretation of these experiments and present results for a large variety of polyatomic molecules, especially substituted benzenes. At densities of vibrational states $> 10^5$ states/cm⁻¹, these molecules show reduced deflection, indicating that statistical rotational motion is a general phenomenon in highly excited polyatomic molecules.

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A comparison between theoretical and experimental state-to-state charge transfer cross sections for $\text{H}^+ + \text{H}_2$ at 20 eV: Evidence for quantum effects

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Charge transfer (CT) is technically important (plasmas, fusion reactors, etc.), and is also of fundamental interest since it is one of the simplest of the electronically nonadiabatic collision processes.¹⁻⁴ Whereas ion-atom CT collisions have been extensively studied, little information is

available for ion-molecule systems. Recently, however, a number of vibrational state-to-state resolved differential scattering experiments have been performed at low energies (< 100 eV).⁵⁻⁷ In the case of the $\text{H}^+ + \text{H}_2$ system,⁵ the new experimental results were compared with classical trajectory

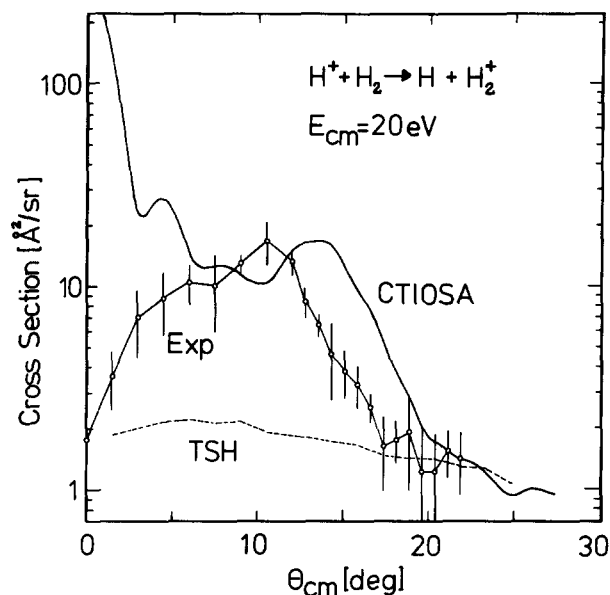


FIG. 1. Comparison of total charge transfer differential cross sections for $\text{H}^+ + \text{H}_2$ at $E_{\text{c.m.}} = 20$ eV. The CTIOSA reproduces the experimentally observed rainbow structure better than the TSH calculations.

surface hopping TSH calculations, a model widely used for dealing with ion-molecule CT collision processes. In this Communication we report on a three-dimensional quantum mechanical close coupling study for this system using the same DIM potential matrix¹ as applied in the TSH calculations (no charge-induced-dipole or induced-quadrupole terms were included in the potential). The new quantum

calculations show a better fit of the experiments than the TSH theory and provide for the first time direct evidence for the use of a quantum treatment in predicting CT processes.

In the experiments the doubly differential cross sections for both collision processes $\text{H}^+ + \text{H}_2(v_i = 0) \rightarrow \text{H}^+ + \text{H}_2(v_f)$ and $\text{H}^+ + \text{H}_2(v_i = 0) \rightarrow \text{H} + \text{H}_2^+(v_f)$ at $E_{\text{lab}} = 30$ eV ($E_{\text{c.m.}} = 20$ eV) and $\theta_{\text{lab}} = 0^\circ - 12^\circ$ ($\theta_{\text{c.m.}} = 0^\circ - 18^\circ$) are measured. One of the most interesting features found is the existence of a clearly assignable rainbow maximum for all inelastic and CT processes at $\theta_{\text{lab}} = 6^\circ - 7^\circ$.

The quantum mechanical treatment was carried out within the infinite order sudden approximation⁸⁻¹¹ which will be denoted CTIOSA.^{12,13} The two electron ($\text{H} + \text{H}_2$)⁺ system is probably more suitable for an IOSA treatment than any other atom-diatom system, because of the nearly isotropic scattering potential. Consequently, the quantum results are largely independent of the fixed orientation assumption implicit in the IOSA. The numerical treatment of the two surface systems is similar to the ones done previously^{12,14} but without the reactive channel.

The total differential cross sections (summed over all final vibrational states) for the CT process are shown in Fig. 1. The two theoretical curves are presented with their absolute scales whereas the experimental one, which is not known absolutely, has been normalized to the CTIOSA curve at the rainbow angle. The fit between the CTIOSA curve and the experimental results is good although the theoretical rainbow is displaced by about 2.5° . A similar displacement was also observed for inelastic scattering in both the TSH (see Ref. 3) and the CTIOSA treatments. Whereas the CTIOSA predicts the primary rainbows, the TSH yields a flat curve which is only slightly dependent on the angle and

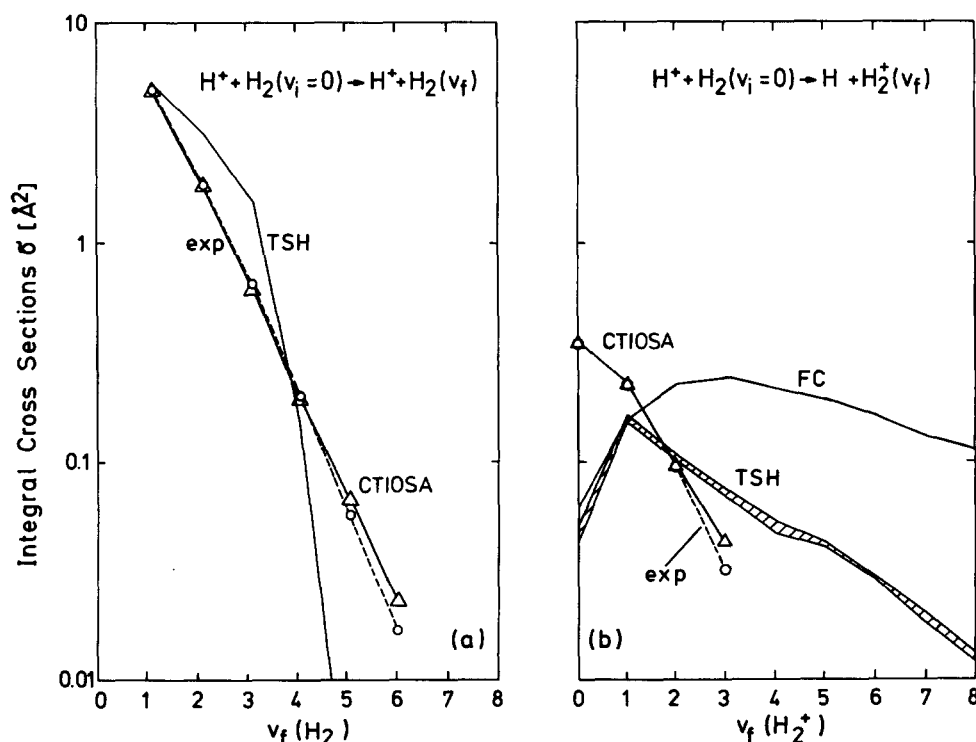


FIG. 2. Comparison of the final vibrational integral cross sections for (a) inelastic and (b) charge transfer processes. The CTIOSA reproduces the experimental results better than the TSH calculations.

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 ClDCI⁻.

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 ClDCI⁻. 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