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A PMO Theory of Gas-Phase Ion−Molecule Collision Rates

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Polarization theory[1−6] has dominated studies of gas-phase ion−molecule collision processes in this century. Langevin published his discussion of ion−molecule kinetic theory in 1905.[1] Polarization theory has expanded and developed; the foundations have not significantly changed.[1−6] Equation 1 gives the Langevin effective attraction potential between a gas-phase ion and a molecule, $V_{eff}(r)$.[1,3,4]

$$V_{\mathrm{eff}}(r) = -q^2\alpha/2r^4 + L^2/2\mu r^2 \qquad (1)$$

r is the distance between the ion and the molecule. μ is the reduced mass. L is the angular momentum of the system. q is the charge on the ion. α is the polarizability of the molecule. Langevin theory assumes that the ion is a point charge, and the molecule is a uniform deformable dielectric.

Proton transfers at distances larger than the calculated cross-section radius were reported by Gioumousis and Stevenson,[3] yet polarization theory was treated as “essentially correct”. The observed rate, k_{obs}, is the product of two factors, the collision rate and the subsequent reaction efficiency. Before the 1990’s, ion−molecule reaction theories usually considered gas-phase proton- and electron-transfer (ET) reactions to have unit efficiency. There was no direct way to check this assumption, since the reaction rate was the only observable.

In a uniform deformable dielectric, the center of the induced dipole would be identical for positive or negative probes at the same distance. This is not true for molecules. Electrons move in response to a charge probe, while the nuclei remain near their original geometry (Born−Oppenheimer approximation). Hydrogen, H_2, reacting with a proton or hydride ion, illustrates differences between molecular polarization responses for positive and negative ions. The geometry of the charge interactions for H_3^+ and H_3^- is different. For a charge and induced dipole, the force varies as $1/r^5$. The distance between the hydride ion and the center of the induced dipole in H_2 will be greater than the distance between a proton and its H_2 induced dipole when both H_3 ion systems have the same nuclear geometry.

More sophisticated theory confirms these results for the forces between a hydrogen molecule and a proton or a hydride. Figure 1a shows a plot of $V(r)$, the Hamiltonian potential ($\int\Psi H_{H_3^+}\Psi^*/\int\Psi\Psi^* - V_{H_2} - V_{H^+}$), against r, the distance between H_2 and H^+, or H_2 and H^-. The plot also shows the polarization potential ($-q^2\alpha/2r^4$), which is the same for both positive and negative ions. The Hamiltonian and polarization curves diverge near 8 Å. The calculations used an STO-3G basis set with Gaussian-92.[7] H_2 bond length was treated as constant. The hydrogen molecule axis was 90° to the line connecting the hydrogen center of mass to the proton or hydride. The Hamiltonian potential for hydride hydrogen is uniformly positive. Figure 1b illustrates the effective potential,[4] $V_{eff}(r)$, for the proton hydrogen collision, at 0.04 eV relative translational energy, in the Hamiltonian and Langevin models (impact parameter, $b_c = 5.6$ Å). The momentum-transfer cross-section radius (b_c) for hydrogen and $Ar^{\bullet+}$ at 0.1 eV collision energy was 5.6 Å.[8] At these distances, the forces between molecules and ions are determined by molecular Hamiltonians, not polarization forces.

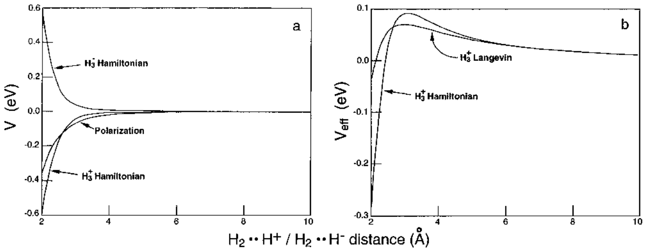

Figure 1. (a) Polarization and Hamiltonian potentials for H^+ and H^- reacting with H_2. (b) Langevin and Hamiltonian centrifugal barriers in the effective potential, V_{eff}, for reaction of H^+ with H_2 (0.04 eV collision energy, $b_c = 5.6$ Å).

Polarization theories of ion−molecule reactions are inadequate because significant orbital overlap occurs at distances greater than the critical radius, $r_c = b_c/2^{1/2}$. The impact parameter, b_c, is the critical separation between the trajectories of the ion and molecule that will result in collision. When the orbitals overlap, the system is described by a molecular wave function. In this wave function, electrons on the ion and molecule exchange, and the polarization approximation fails to describe the forces within the ion−molecule complex.

Perturbation molecular orbital (PMO) theory has potential for development of a robust theory of ion−molecule collisions that is conceptually clear. The theory is applicable to both positive and negative ions. The theory can account for the increased sensitivity of negative ion compared to positive ion mass spectrometry, and high variability of negative ion sensitivity. Relative sensitivity for negative ion spectra is highly variable.[8] The highest mass spectral sensitivity is obtained with negative ion spectra of specific electron capturing molecules.

The first-order attraction potential for a donor, D, and an acceptor, A, one of which is a singly charged ion, is:

$$\Delta E_{\mathrm{DA}} = n_{\mathrm{o}} d_{\mathrm{oD}} a_{\mathrm{oA}} \beta_{\mathrm{DA}} \qquad (2)$$

n_o is the number of electrons in the highest occupied orbital of the ion−molecule complex. a_{oA} and d_{oD} are the frontier orbital coefficients at the bonding site. β_{DA} is the resonance integral for bond formation. The Mulliken approximation[9] for the resonance integral, β_{DA}, is:

$$\beta_{\mathrm{DA}} = cS_{\mathrm{DA}}(IE_{\mathrm{D}} + \mathrm{IE}_{\mathrm{A}})/2 \qquad (3)$$

c is a constant, here it is set to −1. S_{DA} is the overlap integral between the donor and acceptor. For negative ion−molecule complex formation the average of the ionization energies, (IE_D + IE_A)/2, would be the average of the electron affinity of the neutral donor and acceptor. For positive ion−molecule complex formation, the average of the ionization energies would be the average of the ionization energy of the neutral acceptor and donor.

We use spherical Schrödinger-like orbitals ($N_D \exp(-r_D/c_D)$) to represent the highest occupied orbital for the donor and the lowest vacant orbital for the acceptor. We assume that the

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orbital coefficients are unity. c_D is the Bohr radius for an electron on molecule D with orbital energy IE_D. r_D is centered on D. N_D is the normalization constant. S_{DA} (eq 3) has a definite integral for either Schrödinger-like or Gaussian orbitals. The spherical approximation may be extreme for macromolecules that have distinct shapes. It should be reasonable for small molecules. For polar molecules it will be necessary to add a parametric dependence on dipole moment (see average dipole orientation theory[4]).

The PMO ion−molecule potential, $V_{eff}(r)$, is:

$$V_{eff}(r) = \Delta E_{DA} + L^2/2\mu r^2 \tag{4}$$

To avoid the problems associated with numerical solutions of (4), we have adopted the Langevin formal solution as a zero-order approximation.

In polarization theories, the critical value of the interaction radius, $r_c = b_c/2^{1/2}$, is the geometry at which the derivative of the effective potential vanishes ($\delta V_{eff}(r)/\delta r = 0$).[4] We assume that the transition from a polarization force to a Hamiltonian force occurs at r_c, the maxima in Figure 1(b). At r_c the effective potential, $V_{eff}(r)$ of eq 4 equals the relative energy of the system, E_r, in the Langevin theory.[3,4] E_r is the sum of the instantaneous kinetic and potential energies for the system, eq 5. It is the

$$E_r = q^2\alpha/2r_c^{\,4} \tag{5}$$

absolute value of the attractive potential between the ion and molecule in the Langevin model at r_c. The PMO model adopts this formal solution and replaces $-q^2\alpha/2r_c^4$ by ΔE_{DA}.

The PMO collision rate constant for an ion nonpolar molecule pair, k_{PMO}, is

$$k_{PMO} = \upsilon\sigma_c = \upsilon\pi(4r_c^{\,4}*(-\Delta E_{DA})/E_r)^{1/2} = 2\pi(2r_c^{\,4}*(-\Delta E_{DA})/\mu)^{1/2} \tag{6}$$

The term $2r_c^4$ arises from the replacement of the polarization potential by the PMO potential. In this zero-order approximation, $2r_c^4$ is assumed constant for all ion−molecule reactions. We have used the value of $r_c = 1.5$ nm. This value for r_c was arbitrarily selected to maximize the value of the ET efficiency, E_{ET}, when the overlap integral in the Mulliken approximation, δS_{DA}, was approximately 0.001.

In the classical approach the observed rate constant, k_{obs}, is the product of the collision rate constant and an ET efficiency (assumed to be one for exothermic reactions).[4] In this PMO theory E_{ET} is derived[13] from modern electron-transfer theory[10−14] and multiplied by k_{PMO} to obtain the reaction rate. This would not be reasonable for a neutral donor/acceptor complex in solution.[15]

The calculated rate constant for an ion-molecule reaction, k_{calc}, is given by 7.

$$k_{calc} = k_{PMO}*E_{ET} = 2\pi(2r_c^{\,4}*(-\Delta E_{DA})/\mu)^{1/2}*E_{ET} \tag{7}$$

The ET efficiency is the observed reaction rate, k_{obs}, divided by the collision rate, k_{coll}, calculated using PMO theory. E_{ET} can also be obtained by calculation of the rate of electron transfer as a function of the free energy of reaction[10−12] divided by the maximum value for the rate−energy relationship.[13]

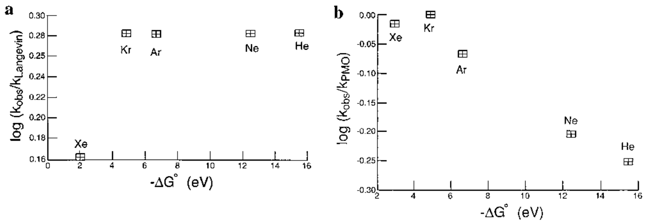

Figure 2. Logs of relative electron-transfer efficiencies, k_{obs}/k_{coll}, in the (a) Langevin and (b) PMO collision models for ET from 1,4-difluorobenzene to rare gas ions (T = 300 K, r_c = 1.5 nm, S_{DA} = 0.0011)

PMO theory explains the differential sensitivity of positive and negative ion mass spectrometry. Negative ions can form by interaction of low-energy electrons and molecules (resonance capture and dissociative capture). The de Broglie wavelength of a thermal electron at 300 K is 7.63 nm, ten times the radius of the highest energy molecular orbital of a small molecule-ion. For resonance electron capture, only the electron affinity of the molecule and the overlap integral for the lowest vacant orbital and the free-electron wave function[16] are involved in $V_{eff}(r)$. The free-electron overlap integral with the lowest vacant orbital of a small molecule will increase as the cube of the de Broglie wavelength. The difference in overlap integrals for free electrons compared to atomic or molecular ions accounts for the high sensitivity of negative ion mass spectrometry.

The variability of negative ion sensitivity is the result of the large variations in electron affinity. Molecules with negative electron affinity, e.g., benzene, will be transparent as molecules, to negative spectra.

Application of this model to electron-transfer reactions[5] is illustrated in Figure 2. Figure 2a shows log $k_{obs}/k_{Langevin}$ for electron transfer from 1,4-difluorobenzene to rare gas ions. Since the rate of electron transfer was assumed to be collision controlled (reaction efficiency unity), the approximate straight-line relationship, zero slope, for log $k_{obs}/k_{Langevin}$ with $-\Delta G°$ was viewed favorably.[5] In Figure 1 the maximum in the V_{eff} curve occurs at a smaller value of r for the Langevin potential than the Hamiltonian potential. The smaller value of r_c for the Langevin curve means that the calculated collision rate would be smaller than that calculated by a Hamiltonian.

Modern electron-transfer theory[10−14] requires that the relationship between the log of the rate of electron transfer and $-\Delta G°$ be more complex than a straight line with zero slope. Figure 2b shows log k_{obs}/k_{PMO} for the same reaction as in Figure 2a (parameters are listed in the figure legend). The plot suggests that the electron-transfer processes from 1,4-difluorobenzene to noble gas ions lighter than xenon are all in the inverted region. Electron transfer to the xenon cation is probably in the inverted region,[17] since the process is exothermic by 3 eV. Electron transfer to these rare gas ions seems to involve excited electronic states of the product ion (compare Figure 2b with figures in ref 17). This is reasonable, in view of reports of photon emission from electron-transfer reactions less exothermic[18,19] than 3 eV.[5]

Inverted-region electron-transfer processes in the gas phase should provide tools for both theoretical and experimental investigations of electron transfer.

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