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Theory of Dissociative Recombination in Vibrationally Excited Gases

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For diatomic ions with large room-temperature recombination rates α, the simple temperature dependence

$$\alpha = CT_{\mathrm{el}}^{-1/2}[1-\exp(-h\nu/kT_{\mathrm{ion}})]$$

is derived, which reproduces closely the precise experiments of Cunningham and Hobson, and others as well. The derivation uses the electronic threshold law plus a rapid fall off of the cross sections with vibrational state v.

The experimental results of Cunningham and Hobson,[1] giving the temperature dependence of the reaction rate for dissociative recombination (DR) for neon and argon, go a long way towards resolving the apparent discrepancy between the $T^{-1/2}$ behavior observed by Biondi *et al.* when only the electrons were heated,[2] and the $T^{-3/2}$ which generally seemed to result when both ions and electrons are heated to 1000°K or more.[3] The turnover of the neon and argon curves[1] from a $T^{-3/2}$ to $T^{-1/2}$ dependence at somewhere below a thousand degrees bridges the gap between the different sets of results, indicating that they are consistent. It further strongly suggests[3] that the $T^{-1/2}$ corresponds to ions in their ground vibrational state, while the transition to the steeper slope is due to vibrationally excited states. It is the purpose of the present paper to find the conditions under which this over-all behavior can be predicted theoretically to analyze the physics and to deduce the appropriate formula.

The reaction rate α follows from the cross sections by the general relation

$$\alpha = \langle \sigma v_{\mathrm{el}} \rangle , \tag{1}$$

where v_{el} is the electron velocity. The average is over a distribution (thermal) of electron and ion states. If σ is taken as the *total* cross section, then electron orientation is already averaged over leaving a distribution over electron energy E_{el} and over the ion states. We further assume that rotational averaging has also been carried out,[4] leaving only an explicit average over vibrational states v, in addition to E_{el}. The reaction rate α is accordingly written

$$\alpha = (1-e^{-h\nu/kT_i})\sum_{v=0}^{\infty} \alpha_v\, e^{-h\nu v/kT_i} , \tag{2}$$

where

$$\alpha_v = \int_0^{\infty} dE_{\mathrm{el}} E_{\mathrm{el}}^{1/2} N e^{-E_{\mathrm{el}}/kT_{\mathrm{el}}} \sigma_v(E_{\mathrm{el}}) v_{\mathrm{el}} . \tag{3}$$

N, the Boltzman normalization factor is equal to $2\pi^{-1/2}(kT_{\mathrm{el}})^{-3/2}$ and contains a spurious $T^{-3/2}$ factor as was pointed out by Bates and Dalgarno.[5] T_{i} and T_{el}, the ion and electron temperatures, are treated as independent variables, in order to investigate the role of each.

Since the behavior of $\alpha(T)$ depends through (2) and (3) on the DR cross section $\sigma_v(E_{\mathrm{el}})$, the principal equations describing DR are, in the next paragraph, collected together from several sources in the form in which they will be used.

DISSOCIATIVE RECOMBINATION THEORY

Dissociative recombination (DR) ($e + AB^{+} \rightarrow A^{*} + B$) is identical with dissociative attachment,[6] (DA) except for the presence of a Rydberg series of neutral states converging to the positive ion's ground state [see Fig. 1(a)]. These states are crossed by the final quasistationary state's curve V_f as it dissociates into the final products $A^{*} + B$. The T matrix for recombination, both exactly and with the same adiabatic[7] approximations as for DA, is one of the form[6]

$$T_{\mathrm{DR}} = \langle \Phi_p^{-} H \phi_r \chi_r^{+} \rangle \simeq \int d\vec{\mathrm{R}}\, \chi_{v_0 J_0}(\vec{\mathrm{R}}) V(\vec{\mathrm{R}}) \chi_r{}^{+}(\vec{\mathrm{R}}) , \tag{4}$$

where Φ_p is the full homogeneous "potential scattering" state,[6] ϕ_r the quasistationary state, $V(\vec{\mathrm{R}})$ the electronic matrix element, and v_0, J_0 are the initial vibrational and rotational quantum numbers. But now the final-state nuclear wave function $\chi_r(\vec{\mathrm{R}})$ is given, because of the Rydberg states n, by a set of coupled equations, previously derived,[8] which may be rewritten in the form

$$[T+V_r(R)+\Delta-\tfrac{1}{2}i\Gamma_a-E]\chi_r(\vec{R})$$
$$=-\sum\nolimits_n V_{nr}(R)\chi_n(\vec{R}), \qquad (5)$$
$$[T+V_{nn}(R)-E]\chi_n(\vec{R})=-V_{nr}(R)\chi_r(\vec{R})\ .$$

Equations (5) determine the desired χ_r and the χ_n. The sum is over the discrete Rydberg states n. The level shift and width operators Δ and Γ have the identical meaning as for DA, incorporating the coupling to the continuum only. They are again approximately local,[6,9] except for Γ when $E_{\rm el}+E_v$ is less than 1 or 2 vibrational quanta $h\nu$.[10] With this modified definition for χ_r and the same semiclassical approximations, the total cross section assumes the same form as for attachment[6] and may be written

$$\sigma_v(E_{\rm el})=C_{\rm FC}(v,E_{\rm el})e^{-\rho(v,E_{\rm el})}\sigma_{\rm el}(E_{\rm el})\ . \qquad (6)$$

Here $C_{\rm FC}$ is the Franck-Condon factor, written $\pi^{1/2}|\tilde{\chi}_r|^2$ in Ref. 6 (here normalized to a maximum value of 1 for $v=0$); $e^{-\rho}$ is the survival factor; ρ is twice the imaginary part of the average final-state eigenphase shift δ_J, from Eq. (5). $\sigma_{\rm el}$ comprises the remaining factors of Ref. (6)

$$\sigma_{\rm el}=(4\pi^{3/2}/k_{\rm el}^{2})g\Gamma_a/\Gamma_d, \qquad (7)$$

where $k_{\rm el}$, g, Γ_a, and Γ_d are, respectively, the electron wave number ($k^2=2mE/\hbar^2$), the spin weighting factor, the autoionization width, and a width for dissociation.

DERIVATION OF TEMPERATURE DEPENDENCE

Consider first the dependence of α or the α_v Eq. (3) on $T_{\rm el}$. The threshold law[11] for an exothermic process in the presence of an initial attractive Coulomb field, as the initial energy ($E_{\rm el}$) approaches zero, is

$$\sigma_{\rm el}\sim\sigma' E_{\rm el}^{-1}+O(E_{\rm el}^{0}); \qquad (8)$$

from (7) this implies that

$$\sigma'=4\pi^{3/2}(\hbar^2/2m_e)g\Gamma_a/\Gamma_d\sim\text{const.}$$

The other two factors approach constant values, but without the same simple power series expansion. By substituting (8) into (6) and into (3), we find the threshold behavior

$$\alpha_v\sim C_v T_{\rm el}^{-1/2} \qquad (9)$$

plus higher-order terms. Now if T_i is kept very small, as in the work of Biondi *et al.* while $T_{\rm el}$ alone is raised, it follows at once from (9) and (2) that $\alpha=\alpha_0\sim C_0 T_{\rm el}^{-1/2}$, in agreement with what was observed,[2] and with the older theory.[5] In terms of the basic parameters,

$$C_0=4(2\pi m_e k)^{-1/2}\sigma'$$
$$=8\pi(m_e k)^{-1/2}g(\hbar^2/m_e)\Gamma_a/\Gamma_d\ .$$

(Note that the small deviation of the exponent from $\frac{1}{2}$ in the experiments[2] has been explained by Bardsley[12] as being simulated by the $E_{\rm el}$ variation first of $C_{\rm FC}$ for a curve crossing to the right or left of the ground-state minimum, and secondly by that of ρ.)

The most general dependence of α on T_i through the v dependence of $C_{\rm FC}$ and ρ (Eqs. 2, 3, and 9) is not well defined, since $C_{\rm FC}$ may either increase or decrease with v. However, there is a special class of systems whose DR rate is large enough to have been observed experimentally near room temperature (e.g., $\mathrm{Ne_2^+}$, $\mathrm{Ar_2^+}$, $\mathrm{Kr_2^+}$, $\mathrm{NO^+}$, etc.). These systems (unlike $\mathrm{H_2^+}$) are observable because a dissociating (quasistationary) state crosses the positive-ion curve somewhere in the Franck-Condon region. This means that both $C_{\rm FC}$ and $e^{-\rho}$ are approximately maximal ($\simeq 1$) for $v=0$. We shall refer to these systems as "maximal systems." The cross sections therefore cannot increase significantly with v, but can only decrease. The reasons why they actually do decrease are discussed later. For the present, it is best systematically to put this in the form of a mathematical assumption: We assume that the cross sections σ_v fall off rapidly with v, or more precisely that

$$\sum_{v=1}^{\infty}\alpha_v e^{-h\nu v/kT_{\rm i}}\ll\alpha_0 \quad \text{(assumption).} \qquad (10)$$

Substituting the assumption (10) into Eq. (3) gives immediately the desired dependence of the reaction rate α on $T_{\rm i}$,

$$\alpha\sim(1-e^{-h\nu/kT_{\rm i}})\alpha_0\ .$$

Only α_0 survives, multiplied by a ground-state depletion factor. Finally, with Eq. (9) for α_0 the full result is

$$\alpha\sim C_0 T_{\rm el}^{-1/2}(1-e^{-h\nu/kT_{\rm i}}) \qquad (11)$$

with C_0 given after Eq. (9). The temperature dependence of (11) for small and large $T_{\rm i}$ is trivially seen to be $T_{\rm el}^{-1/2}$ and $T_{\rm el}^{-1/2}T_{\rm i}^{-1}$, respectively.

Equation (11) is the desired result of this paper. For those cases where the assumption (10) of the rapid falloff of the σ_v holds, it gives the threshold dependence on T_{el} and the more complete dependence on T_{i}. For what systems and in what temperature range Eq. (11) holds is most easily and properly decided at present by experiment.

The fact that the experimental cross sections for NO$^+$ behave according to the formula (11) for $T_{\text{i}} = T_{\text{el}}$ was pointed out previously by Hansen,[13] who justified this dependence for NO$^+$ with empirical arguments based on detailed balancing.

Discussion of the result (11) and its relation to the experiments of the preceding paper and to other experiments will be deferred until after a brief discussion showing the reasonableness of assumption (10), and how it tends to be satisfied generally for the class of systems under discussion.

THE FALLOFF OF σv WITH v FOR MAXIMAL SYSTEMS

It is the purpose of this portion to show that the assumption (10) tends to be satisfied for the physically interesting class of maximal systems (see Fig. 1), for which $C_{\text{FC}} \simeq e^{-\rho} \simeq 1$ when $v = 0$. We now show how both factors tend to fall off monotonically with increasing v, in agreement with the discussion of Mehr and Biondi.[2]

The Franck-Condon factor C_{FC} can be written[6] $\pi^{1/2}|\tilde{\chi}_v|^2$, where the tilde indicates that the vibrational wave function χ_v is distorted and evaluated not at the turning point R_E (Fig. 1) but at the capture point R_{cap}, which satisfies the FC principle and is the same for all v. The variation of C_{FC} with v may therefore be estimated for these systems by comparing the values $|\chi v|^2{}_{\text{av}}$ for normalized harmonic oscillator wave functions, averaged about the equilibrium point ($\simeq R_{\text{cap}}$). A numerical analysis of this quantity shows that roughly

$$C_{\text{FC}} \simeq (1+7v)^{-1/2} \tag{12}$$

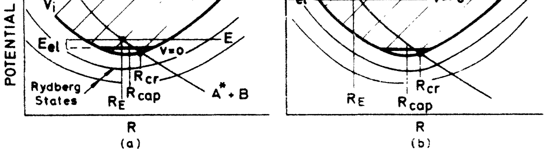

FIG. 1. Typical potential curves V_i and V_f for a maximal system, showing the movement of the turning point R_E with v. The relative positions of R_E and R_{cr} (the crossing point) determine the survival factor $e^{-\rho}$, with the lowest Rydberg states also contributing (Eq. 5). The capture point R_{cap} is independent of v.

for all v. This is a good falloff but not enough to fully satisfy Eq. (10) for large T_{i}. Analytically the falloff should be at least v^{-1} for larger v. Fortunately $e^{-\rho}$ also falls off with v as is now shown.

The survival factor $e^{-\rho}$ for constant E_{el} also decreases monotonically with v. By comparing Fig. 1(a) with 1(b), we see that, as v is increased, the turning point R_E on the dissociating curve V_f moves steadily away from the crossing point R_{cr}. This increases the path over which autoionization is possible and therefore increases ρ. For dissociative attachment, ρ was shown[14] to be given to a good semiclassical approximation by the expression

$$\rho_{\text{DA}} \simeq \int_{R_E}^{R_{\text{cr}}} \hbar^{-1}\Gamma_a(R)\,dt(R),$$

plus small correction terms, where t is the classical time of dissociation. With Γ_a approximately constant (as it is for DR), treating the two potential curves V_i and V_f in Fig. (1) as parabola and straight line reduces this to

$$\rho_{\text{DA}} \simeq 2(\Gamma_a/\Gamma_d)(2v+c)^{1/2}, \tag{13}$$

where $c(\simeq 1)$ depends on E_{el} and on the precise geometry. Equation (13) is an overestimate[10] of ρ_{DA} for $v = 0$, but rapidly becomes accurate as v increases.

The combination of (12) and (13) gives a measure of the falloff of σ_v with v for maximal systems. Comparing (13) with (7) shows that ρ_{DA}, like σ and therefore α, is proportional to Γ_a/Γ_d; thus it may be estimated given α. From (11), the small T_{i} relation is

$$\Gamma_a/\Gamma_d = (kT)^{1/2}\alpha/(8\pi g)$$

with everything in atomic units. Using this relation for neon and argon together with the rough guess $g \simeq \frac{1}{2}$ (this limits the accuracy to 50%), the experiments of Ref. (1) indicate that Γ_a/Γ_d is equal to 0.07 and 0.26 for Ne and Ar, respectively. This, with Eqs. (13) and (12), gives a fast falloff with v for argon but a slower one for neon. However, as mentioned above, the formula for ρ_{DA} neglects the one and only special property of DR, namely coupling to the Rydberg states through Eq. (5). This coupling can only increase $\rho(\rho_{\text{DR}} > \rho_{\text{DA}})$. An assumed factor of 2 increase could make the neon cross sections falloff just about fast enough, when combined with (12), to be consistent with (10).

The Cunningham and Hobson experiment, showing the behavior (11), is taken as an experimental proof that for neon and argon the σ_v do in fact fall off rapidly, at least for the first three or four states.

TEMPERATURE DEPENDENCE FOR OTHER (NONMAXIMAL) SYSTEMS

For ions (like H_2^+) which have no curve crossing near the FC region, the behavior of σ_v will be directly opposite to the assumption (10). C_{FC} will be vanishingly small for low v, and therefore (11) will not hold. The most plausible model of σ_v for such systems, consistent with the foregoing discussion, would be a δ-function model

$$\sigma_v \simeq \delta_{vv'}\sigma_{v'}, \quad (v' \gg 0) .$$

Using this and (9) in (2) leads to the temperature dependence

$$\alpha \simeq C_0 T_{el}^{-1/2}(h\nu/kT_i)e^{-h\nu v'/kT_i} .$$

Even for maximal systems, there are generally one or more additional dissociating states lying within 1 eV of the main one. Each such state makes its own contribution to α, following the Arrhenius-type formula of the last paragraph, with a moderate value of v . At temperatures of many thousand degrees therefore, a second state of this type might become significant, shifting α toward a higher $T^{-3/2}$ curve.

CONCLUSIONS

Under the assumption or model (10) that the cross sections σ_v fall off rapidly with v (ground-state model), using the electronic threshold law, the formula (11) was derived for the dependence of the reaction rate α on T_{el} and T_i. A partial justification of (10) was given for maximal systems.

The experiments of Cunningham and Hobson (preceding paper[1]) which were done with $T_i = T_{el} = T$, follow the formula (11) very closely from the high-temperature $T^{-3/2}$ region right through to the low-temperature $T^{-1/2}$ region, as do those of Biondi *et al.* approximately (see above) with T_i small. It is expected that a number of systems in addition to Ne_2^+, Ar_2^+, and NO^+ will satisfy the assumption (10), and therefore have the temperature dependence (11).

Finally, the small observed deviation[2] of the exponent of T_e from $-\frac{1}{2}$, due to the E_{el} dependence of C_{FC} and ρ[12], would require that Eq. (11) be modified to

$$\alpha \approx C_0' T_{el}^{-\gamma}(1-e^{-h\nu/kT_i})$$

with $\gamma = 0.5 \pm 0.2$. This is a further refinement not pursued here.

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