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SCALING LAWS FOR INELASTIC COLLISION PROCESSES IN DIATOMIC HALOGENS

by

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SCALING LAWS FOR INELASTIC COLLISION PROCESSES IN DIATOMIC HALOGENS

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I. INTRODUCTION

The past two decades have witnessed the development of highly specific and selective methods for molecular quantum state preparation and detection. With these techniques, a large number of data is potentially available on state-to-state kinetic processes in simple diatomic molecules, such as the halogens. Indeed, a recent survey of the latter systems [1] includes nearly 2,000 measurements of rates and/or cross-sections for inelastic collision processes.

It is generally acknowledged that these data are not all independent; on the contrary, rates for processes which differ only slightly in initial and/or final state should be closely correlated. In principle, such correlations

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could be derived ab initio from formal scattering theory. While straightforward, such calculations are quite tedious, especially for heavy systems (such as I₂) and large quantum numbers. Classical trajectory calculations have been performed [2] but require sampling over a wide range of initial conditions to be accurate. Quantum close-coupled calculations are feasible only for low j states, due to the rapidly expanding size of the matrices involved. In either case, an accurate intermolecular potential function is required if the calculations are to yield meaningful results; such potentials are by no means well known, particularly if one of the collision partners is in an electronically excited state.

For these reasons, a number of attempts have been made during the past several years to find semi-empirical systematizations or condensations of such data, in which a small number of measured data would suffice to determine an entire state-to-state array. One general formulation for carrying this out is the so-called "surprisal analysis," based on the entropy maximization principle of information theory [3]. This analysis, applied to rotation-vibration energy transfer data in I₂⁺ [4], appeared to give a satisfactory representation of the data. More recently, however, Pritchard, et al. [5] have suggested that their data on rotational energy transfer in Na₂⁺ are better represented by a power law than by the exponential-gap law predicted by information theory. A theoretical basis for the power law has been given by De Pristo, et al. [6] who derived infinite-order sudden (IOS) and energy-corrected sudden (ECS) scaling laws from quantum-mechanical scattering theory.

The purpose of this report is to test the various scaling laws proposed for inelastic collision rate coefficients, using the information available in the survey of data for the diatomic halogens [1]. In addition, we will also investigate a scaling law proposed for intermolecular potentials, i.e.,
varying collision partner [7]. Section II of this report summarizes the various energy/angular momentum scaling laws. Section III gives the fits obtained with these laws for $I_2^*$ in various initial $v,j$ states and with various collision partners. In Section IV, we discuss several applications of the intermolecular potential scaling law.

II. ENERGY AND ANGULAR MOMENTUM SCALING LAWS FOR INELASTIC PROCESSES

1. The exponential gap law (EGL) is based on the maximum entropy principle of information theory [3]. The inelastic collision rate connecting initial vibration-rotation state $(v,i_l)$ with final state $(v_f,j_f)$ is written as

$$ k(v_i j_l + v_f j_f ; T) = A(T) k^0(v_i j_l + v_f j_f ; T) \exp[\frac{\lambda}{kT}] $$

with the "prior" or statistical rate given by

$$ k^0(v_i j_l + v_f j_f ) = \frac{r^0 \mu^{3/2}}{\pi^{5/2} \hbar^3} \frac{(2j_f + 1)}{\Delta E} \frac{\Delta E}{kT} \frac{\Delta E}{kT} K_1(\Delta) $$

In Equation (2), $\Delta = (E_i - E_f)/2kT$ (the energies are calculated from spectroscopic term values), and $K_1(\Delta)$ is the modified Bessel function of the first order and second kind [8]. These equations can be written compactly as

$$ k_{EGL}(v_i j_l + v_f j_f ) = a e^{-\theta |\Delta E|} (2j_f + 1) \Delta E K_1(\Delta) $$

with fitting parameters $a$, including all constants and scale factors, and $\theta = \lambda/kT$.

The $v_i = v_f$ (pure R-T) process is just a special case of the general EGL. This scaling law can also be applied to pure V-T processes by summing the
prior rates over $j_f$. This gives [3]

$$k_{ECL}(v_1^*, v_f; T) = \exp\left[-\lambda \nu_n |E_{v_1} - E_{v_f}|/kT\right] \Delta^{2} e^{\Delta K_2(\Delta)} \tag{4}$$

where $K_2(\Delta)$ is the modified Bessel function of the second order and second kind [8].

2. **The statistical power-gap (SPG) [5] scaling law** is an empirical power-law in $\Delta E$ having the form

$$k_{SPG}(v_1^*, j_1^*; v_f^*, j_f^*) = a \left| \frac{\Delta E}{B} \right|^{-\alpha} N_{\lambda}(j_1^*, j_f^*) \Delta e^{\Delta K_1(\Delta)} \tag{5}$$

The differences between ECL and SPG are (i) fitting is with a dimensionless parameter $\alpha$ (this can be obtained from the ECL by applying entropy maximization to $\ln|\Delta E|$ instead of to $|\Delta E|$); (ii) angular momentum restrictions are imposed via the factor $N_{\lambda}$ (which reduces to $2j_f + 1$ in the limit of large $\lambda$).

Again, this fitting law should encompass both pure R-T ($v_1^* + v_f^*$) and mixed V,R-T ($v_1 j_1^* + v_f j_f^*$) processes. The sum over $j_f$ for V-T processes gives

$$k_{SPG}(v_1^*, v_f^*) = a \left| \frac{\Delta E}{B} \right|^{-\alpha} \Delta^{2} e^{\Delta K_2(\Delta)} \tag{6}$$

3. **Angular-momentum based scaling laws.** In contrast to the preceding scaling laws, which are based on the amount of energy transferred, are the expressions based on the sudden approximation in inelastic scattering theory [6], which have been used successfully to analyze data for $Na_2^* - M$ collisions [5] and other systems. The energy-corrected sudden (ECS) scaling law for a transition from initial rotational state $j_1$ to final state $j_f$ is given by
\[ k_{\text{ECS}}(j_1^e + j_f) = (2j_f + 1) \exp \left[ \frac{E_{j_1^e} - E_{j_f}}{kT} \right] \times \left[ \begin{array}{cc} j_1^e & j_f \\ j_1^e & j_f \end{array} \right] \left( \begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array} \right) (2\ell + 1) [A_{\ell}^{j_1^e}]^2 k(\ell + 0) \]

(7)

where the symbols have the following meanings: \( j^e_1 = \) larger \((j_1^e, j_f)\); \( F_{j_1^e}, F_j \) to be calculated from spectroscopic term values; \( T \) = ambient translational temperature; \( \left( \begin{array}{c} * \\ * \end{array} \right) = 3-j \) symbol;

\[ A_{\ell}^{j_1^e} = \frac{1 + \frac{\tau_2^2}{6}}{1 + \frac{\tau_2^2}{j^e_1}} \]

(8)

\[ \tau_j = 4\pi c B(j_1^e + 1/2)/\bar{v} \] where \( \bar{v} \) = mean thermal relative velocity; \( R \) = rotational constant in \( \text{cm}^{-1} \); \( k(\ell + 0) = a[\ell(\ell + 1)]^{-\gamma} \). The parameters \( a, \gamma, \) and \( \ell_c \) are used for the fit; the sum over \( \ell \) can be taken over \( |j_1^e - j_f| < \ell < |j_1^e + j_f| \) with sufficient accuracy. If \( \ell_c \) is set equal to zero, the quantity \( A_{\ell}^{j_1^e} \) equals one, and the infinite-order sudden (IOS) scaling law is obtained.

For collisions between heavy diatomic molecules (e.g., \( I_2^* \)) and light collision partners (e.g., \( \text{He} \)), it may be necessary to restrict the amount of angular momentum which can be transferred. This has been done by modifying the form of \( k(\ell + 0) \) as follows,

\[ k(\ell + 0) = a[\ell(\ell + 1)]^{-\gamma} \exp [-\ell(\ell + 1)/j^* (j^* + 1)] \]

(9)

thereby introducing an additional parameter \( j^* \). An alternative formulation, termed the "AON" scaling law, has recently been derived [9]:

\[ k(\ell + 0) = c[(\frac{a}{n}) \log(\frac{a}{n}) - (\frac{a}{n})^2 + 1] \]

(10)

where \( n = \ell \) for a heteronuclear diatomic molecule, \( n = \ell/2 \) for a homonuclear diatomic molecule, and the only fitting parameters are the overall scale.
factor \( c \) (replacing \( a \) in Eq. (9)) and the nonlinear parameter \( \alpha \), which incorporates the information contained in \( \gamma \) and \( \xi^* \).

The ECS (IOS) really applies only to pure R-T transfer (\( j_1 \leftrightarrow j_f \) at constant \( v \)). For mixed \( V-T + R-T \), the appropriate ECS law has been given in the articles by De Pristo [6,10]:

\[
k_{\text{ECS}}(v_{1j_1} \leftrightarrow v_{fj_f}) = (2j_f + 1) \exp\left[ -\frac{\Delta(v_{1j_1} \leftrightarrow v_{fj_f})}{kT} \right]
\]

\[
\times \sum_{m,l} \left( \begin{array}{cccc} j_1 & j_f & \xi^* & 2 \\ 0 & 0 & 0 & 0 \end{array} \right) \frac{v_{1j_1}v_{fj_f}}{m} \left| A(\xi^*|00) \right|^2 k_{m\xi+00}
\]

(11)

with

\[
\Delta(v_{1j_1} \leftrightarrow v_{fj_f}) = \left\{ \begin{array}{cc} E_{v_{1j_1}} - E_{v_{1j_1}} & E_{v_{1j_1}} < E_{v_{fj_f}} \\ 0 & E_{v_{1j_1}} > E_{v_{fj_f}} \end{array} \right.
\]

There are several problems in implementing this fit. First, the \( |I|^2 \) factor requires integration over rotating anharmonic oscillator wavefunctions. While these expressions are available in Ref. [6], the actual computation is quite tedious. Second, it is entirely possible to have a different \( \xi^* \) parameter, appearing in the factor \( |A(\xi^*|00)/A(v_{1j_1} \leftrightarrow v_{fj_f})|^2 \), for each value of \( v_f \). This makes the fitting procedure somewhat arbitrary. Finally and most problematical, one needs to have basis rates \( k_{m\xi+00} \) for high-\( m \) oscillator states. For these reasons, the application of Eq. (11) to the severely limited number of \( V,R-T \) data sets is of doubtful practical utility.
Before leaving this topic, it may be instructive and even useful to estimate the magnitudes of some of the quantities appearing in the ECS. Consider in particular the adiabatic correction term $1 + \tau_j^2/6 = 1 + (\omega_j T_d)^2/6$, appearing in Eq. (8). Consider $I_2^*(v)$ in high-$v$, low-$j$ ($v = 43, j = 12$) and low-$v$, high-$j$ ($v = 14, j = 100$) states, with

$$B_v = 0.022 \text{ cm}^{-1}(v = 43), \ 0.0267 \text{ cm}^{-1}(v = 14).$$

$$\omega_j = 4\pi c B_v(j+1/2) = 1 \times 10^{11} \text{ radians sec}^{-1} (v = 43, j = 12)$$

$$= 1 \times 10^{12} \text{ radians sec}^{-1} (v = 14, j = 100).$$

Thus, the angular velocity of a rotating $I_2$ will be in the range $10^{11}$-$10^{12}$ radians/sec.

For $T_d = \ell_c/\bar{v}$, take $\ell_c = 1 \text{ Å} = 10^{-8} \text{ cm}$

For $I_2^*-$He, $\bar{v} = 1.27 \times 10^5 \text{ cm sec}^{-1}$, $T_d = 8 \times 10^{-14} \text{ sec}$

For $I_2^*-$Xe, $\bar{v} = 2.7 \times 10^4 \text{ cm sec}^{-1}$, $T_d = 3.7 \times 10^{-13} \text{ sec}$

So let us make a little table covering the possible range of the factor $1 + \tau_j^2/6$:

<table>
<thead>
<tr>
<th></th>
<th>$\omega_j = 10^{11} \text{ sec}^{-1}$ (low $j$)</th>
<th>$\omega_j = 10^{12} \text{ sec}^{-1}$ (high $j$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2^*-$He</td>
<td>1.00001</td>
<td>1.001</td>
</tr>
<tr>
<td>$I_2^*-$Xe</td>
<td>1.0002</td>
<td>1.023</td>
</tr>
</tbody>
</table>

Thus, this factor is very close to 1, and the IOS should in fact be a good approximation for most $I_2^*-$M collisions. The worst case is for high-$j$ states with heavy collision partners ($I_2^*-$Xe, $I_2^*-$I$_2$), and even then the correction per term is only a few per cent.
III. RESULTS OF FITTING TO SCALING LAWS

The algorithms for fitting the scaling-law parameters were first tested with the rotational energy transfer (RET) data of Dexheimer, et al. [11] for $I_2^*(v_1=13, j_1=41, 81, 91, \text{ or } 113) + M(=\text{Xe, He})$. The results for xenon are shown in Table 1. The entries labelled "D^2BP" refer to the fits published in Ref. 11, while "JILA" refers to those computed using our programs. The correspondence is indeed quite close, with the exception of the SPG, for which the value of the parameter a published in Ref. 11 is off by a factor of 23 due to a programming error [12]; the value given in Table 1 is the correct one. Note that for the IOS and ECS scaling laws in particular, the actual values of the parameters can vary by as much as ±10% and still give equivalent fits; this implies that too much physical significance should not be attributed to the precise value of these parameters. The AON fitting law, as recomputed by us, seems to be about as good as the SPG for this system. The data and the corresponding fits are shown in Figs. 1-4. Similar agreement was also obtained for the $I_2^*-\text{He}$ data of Ref. 11.

The scaling laws were next applied to the RET data on $I_2^*(v_1=25, j_1=34) + M$, [13] which had earlier been used to validate the EGL or "surprisal" analysis [4]. The results are given in Table 2. The smaller values of $\chi^2/\nu$ for the EGL, as compared with Table 1, simply reflect the lower precision of the earlier measurements. Use of the unadorned IOS or ECS scaling laws [Eq. (7)] actually give worse fits; when these are modified according to the angular-momentum restriction given by Eq. (9), significantly improved fits are obtained. The results for $I_2^*-^4\text{He}$ are shown in Figs. 5-8, and those for $I_2^*-^3\text{He}$ in Figs. 9 and 10. We conclude that angular-momentum-based scaling laws are indeed the correct ones to use for RET, and should be employed whenever such data are to be described.
A comment may also be made about the parameter $j^*$, appearing in Eq. (9). Representing as it does a limit on the number of angular momentum quanta which can be transferred in a collision, $j^*$ should be comparable with the orbital angular momentum available in the collision. A typical value for this quantity can be estimated as

$$\bar{\ell} = \mu \tilde{v} b / \hbar$$  \hspace{1cm} (12)$$

For $I_2^* - ^4\text{He}$, the reduced mass $\mu = 3.95$ atomic units ($m_H = 1.008$), $\tilde{v} = 12.7 \times 10^4 \text{ cm sec}^{-1}$ at 298 K, and we can take an average impact parameter $b = 4 \times 10^{-8} \text{ cm}$. These values, inserted in Eq. (12), give $\bar{\ell} = 31.6$; the closeness of this value to the fitted parameter $j^* = 31.7$ is, of course, fortuitous. The magnitude is physically correct, though. For $I_2^* - ^3\text{He}$ collisions, $\bar{\ell}$ should be reduced by a factor $(3/4)^{1/2}$ to give 26, and the parameter fit $j^* = 20$ is in the right direction. For collisions with $\text{Xe}$, $\bar{\ell}$ or $j^*$ would be approximately 150, and a reduction factor of $\exp[-\bar{\ell}(\ell+1)/j^*(j^*+1)]$ would not be noticeable. We may also note that this relationship was suggested in the early work on RET in $I_2^*$ [Ref. 13].

Scaling laws were also tested for the $I_2^*-I_2$ and $I_2^*-\text{Kr}$ RET data of Ref. 13. These results are given in Table 2, and are shown in Figs. 11 and 12. For the ECS and IOS laws, it was necessary to restrict the range of fitted data points to $|\Delta j| < 24$, probably reflecting inaccuracy of the measurements for large $\Delta j$. Within this restricted range, the angular-momentum based scaling laws (ECS, IOS, or AON) are once again acceptable. A point of interest is that this remains valid for collisions with a diatomic collision partner ($I_2$) nearly as well as for monoatomic inert gases.

We may also note that first-order theories of vibrational energy transfer predict a simple scaling law for $\Delta v = 1$ processes as a function of initial
state \( v_1 \), namely,
\[
\sigma(v_1 + v_1 - 1) \propto v_1
\]

This relationship is well illustrated by vibrational deactivation data for \( \text{IF} \) \((B^3 \Pi)\) colliding with helium [15]. Other examples are given in Reference [3].

IV. INTERMOLECULAR POTENTIAL SCALING LAWS

Parmenter and co-workers (LSTKP; Ref. 7) have suggested the following scaling law for \( XY(\Gamma) + M \leftrightarrow XY(\Gamma') + M \) collisions, in which \( \Gamma \) and \( \Gamma' \) may be vibrational, rotational or electronic states of \( XY \):
\[
\ln C_M = \ln c + \beta (\varepsilon_{MM}/k)^{1/2}
\]  
(13)

Thus, knowledge of the Lennard-Jones well depth parameter \( \varepsilon_{MM} \) for the collision partner alone should suffice to determine the relative magnitudes of the (velocity-averaged) cross-sections for the given inelastic process, so long as long-range forces dominate the interaction. Other scaling laws have been proposed [16-18], incorporating various terms in the multipole expansion of the intermolecular potential, but that given by Eq. (13) is the simplest and most straightforward to apply. The slope parameter \( \beta \) is shown in Ref. (7) to have the form
\[
\beta = \left\{ \varepsilon'(XY, \Gamma)/kT^2 \right\}^{1/2}
\]  
(14)

Thus, \( \beta \) contains information about the potential for the diatomic molecule in state \( \Gamma \), and should be inversely proportional to temperature.

Quenching of the \( I_2^* (B) \) state via collision-induced predissociation represents a particularly successful application of these scaling laws. The
data for \( v_1 = 6, 15, 25, 43 \) and 50 (Refs. 19, 20, 13, 14, and 21, respectively) are shown in Fig. 13. Good correlations are obtained in all cases. The slopes of the fitted lines show a noticeable decrease in going from \( v' = 6 \) to \( v' = 50 \); in terms of Eq. (14), this would imply that the attractive potential between an electronically excited I\(_2\) molecule and another particle becomes weaker as the molecule is excited to higher \( v' \) states. A simple model can provide some insight into this behavior. A potential which has been used previously [22] for analysis of I\(_2^\ast\)-M collisions can be represented as a sum of two-body interactions,

\[
V(I_2, M) = V_0(r_0) + V_1(r_1) + V_2(r_2)
\]  

(15a)

with

\[
V_0(r_0) = D_e \left\{ 1 - e^{-2(r_0 - r_e)^2} \right\}
\]  

(15b)

and

\[
V_i(r_i) = \frac{6\epsilon a^6}{\alpha - 6} e^{-\alpha(r_i/r_m)^6} - \frac{\alpha e r^6}{\alpha - 6} r_i^{-6} \quad (i=1,2)
\]  

(15c)

The inter- and intramolecular potential parameters are \( D_e, \beta, r_e, \epsilon, r_m \) and the distances \( R, r_0, r_1, \) and \( r_2 \) are defined in Fig. 14. We want to know how the average I\(_2^\ast\)-M interaction energy, \( \tilde{V}_{\text{eff}}(R) \), depends on \( r_0 \). It is clear from inspection of Fig. 14 that, for configurations in which the particle M is roughly equidistant between the two I atoms, we will have \( r_1' > r_1 \) and \( r_2' > r_2 \) for \( r_0' > r_0 \). But if in addition \( (r_1, r_2) > r_m \) -- that is, if we are dealing with the long-range attractive part of the potentials -- we will then have \( V_1(r_1') < V_1(r_1) \) and \( V_2(r_2') < V_2(r_2) \), so that the net attractive potential decreases at large values of \( r_0 \), which in turn are associated with
the higher v'-levels. This would lead to the correlation shown in Fig. 13. More quantitative molecular-orbital calculations could help elucidate this point.

Vibrational energy transfer is found not to obey the LSTKP correlation [7], presumably because short-range forces dominate this inelastic process. Vibrational relaxation at very low relative kinetic energies in supersonically cooled beams, however, is considered to be dominated by long-range forces [23], and thus the correlation should be applicable. We have tested the two sets of data available for the process, viz., for I₂ [24] and Br₂ [25], each with a variety of collision partners. The data for I₂, shown in Fig. 15, are in excellent agreement with Eq. (13). Those for Br₂, however (Fig. 16), do not obey this correlation at all; indeed, the cross-sections for the monatomic rare gases and for the diatomics (H₂, D₂, N₂, O₂), appear to be anti-correlated with intermolecular potential. A reason for this discrepancy is not immediately apparent.

Finally, let us consider the temperature dependence predicted by Eq. (14). Only a very few data sets are available over a sufficiently wide temperature range to carry out this comparison. Two of these, for quenching I₂*(B³Π) in v₁ = 6 [26] and v₁ = 25 [27], with 300 < T < 650 K, are shown in Fig. 17. It is evident that for this system, at least, the predicted temperature dependence is not observed; indeed, the effective quenching cross sections appear to be essentially independent of temperature.
V. CONCLUSIONS

Accurate scaling laws are available for correlating and/or predicting variations of the rate coefficient or cross section for inelastic collision processes with changes in initial quantum state, final quantum state, or collision partner. In particular, the angular-momentum-based IOS and ECS scaling laws give a good representation of all available rotational energy transfer data. Additional measurements, particularly for heteronuclear species such as the interhalogen molecules, would be highly desirable.

ACKNOWLEDGMENTS

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References


12. D. E. Pritchard (private communication).


15. P. Wolf and S. Davis (private communication).

Table 1.
Comparative fits for
$I_2^* (v_I=13, j_I=41, 81, 91, 113) + Xe + I_2^* (v_f=13, j_f) + Xe$

<table>
<thead>
<tr>
<th>Scaling Law</th>
<th>Parameters</th>
<th>$\chi^2/\nu$</th>
<th>See Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGL-D$^2$BP</td>
<td>$a = 0.125(-12)$, $\theta^{-1} = 63$ cm$^{-1}$</td>
<td>10.42</td>
<td>1</td>
</tr>
<tr>
<td>EGL-JILA</td>
<td>$a = 0.125(-12)$, $\theta^{-1} = 62$ cm$^{-1}$</td>
<td>10.38</td>
<td>1</td>
</tr>
<tr>
<td>SPG-JILA</td>
<td>$a = 0.443(-10)$, $\alpha = 0.866$, $\lambda = 82$</td>
<td>1.14</td>
<td>2</td>
</tr>
<tr>
<td>IOS-D$^2$BP</td>
<td>$a = 0.470(-10)$, $\gamma = 0.873$</td>
<td>2.57</td>
<td>--</td>
</tr>
<tr>
<td>IOS-JILA</td>
<td>$a = 0.423(-10)$, $\gamma = 0.864$</td>
<td>2.25</td>
<td>--</td>
</tr>
<tr>
<td>ECS-D$^2$BP</td>
<td>$a = 0.730(-10)$, $\gamma = 0.911$, $\xi_c = 3.2$ Å</td>
<td>1.20</td>
<td>3</td>
</tr>
<tr>
<td>ECS-JILA</td>
<td>$a = 0.669(-10)$, $\gamma = 0.904$, $\xi_c = 3.16$ Å</td>
<td>1.02</td>
<td>3</td>
</tr>
<tr>
<td>AON-WB$^a$</td>
<td>$a = 54.5$, $c = 0.80(-13)$</td>
<td>8.44</td>
<td>4</td>
</tr>
<tr>
<td>AON-JILA</td>
<td>$a = 107.3$, $c = 1.74(-14)$</td>
<td>2.54</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$ WB = Whitaker and Brechignac (Ref. 9); they fitted $j_I = 41$ data only, and omitted a factor of $10^{-13}$ in the value of $c$ reported in their paper.
Table 2.
Comparative Fits for $I_2^*(v_f=25, j_f=34) + M + I_2^*(v_f=25, j_f) + M$

<table>
<thead>
<tr>
<th>Scaling law</th>
<th>Parameters</th>
<th>$\chi^2/\nu$</th>
<th>See Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGL</td>
<td>$a = 0.0011$, $\theta^{-1} = 16$ cm$^{-1}$</td>
<td>2.4</td>
<td>5</td>
</tr>
<tr>
<td>IOS</td>
<td>$a = 0.9802$, $\gamma = 1.48$</td>
<td>4.6</td>
<td>6</td>
</tr>
<tr>
<td>IOS-$j^*$</td>
<td>$a = 0.2648$, $\gamma = 0.969$, $j^* = 31.7$</td>
<td>0.99</td>
<td>7</td>
</tr>
<tr>
<td>ECS</td>
<td>$a = 0.403$, $\gamma = 1.129$, $\xi_c = -14$ Å</td>
<td>1.98</td>
<td>8</td>
</tr>
<tr>
<td>ECS-$j^*$</td>
<td>$a = 0.3379$, $\gamma = 0.977$, $\xi_c = 37$ Å, $j^* = 34.2$</td>
<td>0.89</td>
<td>8</td>
</tr>
<tr>
<td>AON</td>
<td>$a = 27.9$, $c = 5.41(-4)$</td>
<td>1.65</td>
<td>8</td>
</tr>
<tr>
<td>EGL</td>
<td>$a = 0.00145$, $\theta^{-1} = 14$ cm$^{-1}$</td>
<td>3.15</td>
<td>9</td>
</tr>
<tr>
<td>IOS-$j^*$</td>
<td>$a = 0.0488$, $\gamma = 0.533$, $j^* = 19.9$</td>
<td>2.86</td>
<td>10</td>
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<tr>
<td>ECS-$j^*$</td>
<td>$a = 0.0619$, $\gamma = 0.513$, $\xi_c = 47$ Å, $j^* = 20.7$</td>
<td>2.24</td>
<td>10</td>
</tr>
<tr>
<td>EGL</td>
<td>$a = 0.0024$, $\theta^{-1} = 14.8$ cm$^{-1}$</td>
<td>1.66</td>
<td>11</td>
</tr>
<tr>
<td>ECS</td>
<td>$a = 0.3206$, $\gamma = 0.981$, $\xi_c = 3$ Å</td>
<td>2.6</td>
<td>11</td>
</tr>
<tr>
<td>IOS</td>
<td>$a = 0.3046$, $\gamma = 0.979$</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>AON</td>
<td>$a = 34.0$, $c = 5.83(-4)$</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>EGL</td>
<td>$a = 0.00144$, $\theta^{-1} = 22.1$ cm$^{-1}$</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>ECS</td>
<td>$a = 0.622$, $\gamma = 1.06$, $\xi_c = 7.5$ Å</td>
<td>0.55</td>
<td>12</td>
</tr>
<tr>
<td>IOS</td>
<td>$a = 0.524$, $\gamma = 1.05$</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>AON</td>
<td>$a = 34.3$, $c = 6.28(-4)$</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>

The parameter $a$ (or $c$, for the AON) is in units of cross section ($\text{Å}^2$); to obtain rate coefficients, multiply by $12.7(-12)$. 
Fig. 1. RET data from Ref. 11 for $I_2^* + Xe$ ($v_i=13, j_i=41, 81, 91,$ and $113 \rightarrow v_f=13, j_f$) with EGL scaling law [Eq. (3)].
Fig. 2. Data as in Fig. 1, with SPG scaling law [Eq. (5)].
Fig. 3. Data as in Fig. 1, with ECS scaling law [Eq. (7)].
Fig. 4. Data as in Fig. 1, with AON scaling law [Eq. (10)].
Fig. 5. RET data from Ref. 13 for $I_2^* + ^4\text{He} (v_1=25, j_1=34 \rightarrow v_f=25, j_f)$ with EGL scaling law [Eq. (3)].
Fig. 6. Data as in Fig. 5, with IOS and IOS(j*) scaling laws.
Fig. 7. Data as in Fig. 5, with ECS and ECS(j*) scaling laws [Eqs. (7) and (9)].
Fig. 8. Data as in Fig. 5, with AON scaling law [Eq. (10)].
Fig. 9. RET data from Ref. 13 for $^3$He ($v_i=25$, $j_i=34 + v_f=25, j_f$) with EGL scaling law [Eq. (3)].
Fig. 10. Data as in Fig. 9, with ISO($j^*$) and ECS($j^*$) scaling laws.
Fig. 11. RET data from Ref. 13 for $I_2^* + I_2$ ($v_i=25$, $j_i=34 \rightarrow v_f=25$, $j_f$) with EGL, ECS, and IOS scaling laws.
Fig. 12. As in Fig. 11, for I$_2^*$ + Kr.
Fig. 13. LSTKP plots of quenching cross-sections for $I_2*(B^3\Pi)$ in $v'=6, 15, 25, 43, \text{ and } 50$ (data of Refs. 19, 20, 13, 14, and 21, respectively). Note that the data for $v'=15, 25, 43, \text{ and } 50$ have been rescaled to avoid congestion on the plot.
Fig. 14. Effect of increasing I - I distance on $I_2$-M potential.
Fig. 15. LSTKP plot of vibrational relaxation cross-sections (relative to $\sigma(\text{He}) = 1.0$) for $I_2$ in a supersonic beam (data of Ref. 23).
Fig. 16. LSTKP plot of vibrational relaxation cross-sections for Br₂ in a supersonic beam (data of Ref. 24).
Fig. 17. Temperature dependence of cross-sections for quenching \( I_2*(B^3\pi) \) in \( v_1 = 6 \) and 25 (data of Refs. 25 and 26, respectively).