

Rotational Energy Transfer in $I_2^*(B^3\Pi)$ Colliding with $I_2(X^1\Sigma)$, Ar and He: Experiment and Fitting Law

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Abstract. Using the LIF method, we have measured the rate constants of rotational energy transfer for $I_2^*(B^3\Pi)$ in several rovibrational levels and for changes in j up to 32, with $I_2(X^1\Sigma)$, Ar and He as collision partners. A new approach of data processing has been employed to deduce the rate constants from the experimental data. These rate constants were then correlated with fitting laws. It was found that the $I_2^*-I_2$ and I_2^*-Ar pairs follow the power gap law with the restriction of $\Delta m_j = 0$, but the I_2^*-He system has to be represented by an intermediate case between the power gap and exponential gap laws.

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Collisional energy transfer process in the I₂ molecule has been a subject of interest for many years. This is largely due to the following reasons: 1) The iodine has a high enough vapor pressure of a few hundredths of a torr at room temperatures, which is very suitable for the study of energy transfer processes. Moreover, its commercial sample can be easily obtained with high purity. 2) Iodine fluoresces intensely on the B-Xtransition in the visible region where several common laser sources are available. 3) As the electron-rotation coupling belongs to Hund's case (c), $I_2 B^3 \Pi_0^+$ state is a component of ${}^{3}\Pi$ state with very large splitting. Therefore, it behaves like a ${}^{1}\Sigma$ state rather than a ${}^{3}\Pi$, which makes any transition, starting therefrom, bears a singlet appearance rather than a triplet one although it is denoted symbolically by a triplet state [1].

But as the I_2 molecule in the $B^3\Pi$ state is subject to both spontaneous and collision-induced predissociation, the effective spontaneous lifetime of the excited levels and their dependence on foreign gas pressure are very much complicated and vary greatly for different levels, as a result of curve crossing between the repulsive state and the bound state [2]. A thorough and systematic study of these relaxation pathways and their rates cannot be performed until recently [3]. Therefore, there have been only meager precise measurement on the rotational energy transfer constants, which depend directly on the relaxation rates.

Generally speaking, there always exists multiplecollision effects for collision-induced energy transfer under ordinary experimental conditions. A method usually adopted to eliminate the multiple-collision was proposed by Bergmann and Demtröder [4], while a newer method based on an exact solution of the steadystate rate equation was used in the Na^{*}₂-Xe collision [5]. However, it is handicapped by not considering all the relaxation channels.

Among the many studies on the I_2 molecule, only Dexheimer et al. examined their rate constants of I_2^* -Xe and I_2^* -He with fitting laws and succeeded in getting rid of the multiple-collision effect satisfactorily. They found that the rate constants for I_2^* -Xe collision obeyed the power-gap law, whereas the rate constants for I_2^* -He were best fitted by a complicated fitting law with 5 adjustable parameters [6].

In this letter paper, we report on the study of rotational energy transfer of $I_2^*(B^3\Pi_0^+)$ colliding with $I_2(X^1\Sigma_9^+)$, Ar, and He. The iodine was chosen as a prototype in the hope of improving over the study of

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the previous authors. The reason of choosing these collision partners was that we wish to compare our results with those of Dexheimer. An OMA-2 system was emplyed as the signal detector in order to eliminate the effect of laser fluctuation. In the data reduction, we adopted the technique proposed by Brunner et al. [5] to deduce the actual intensity ratio *T*, together with a method by combining least-squares-fits with an iterative process to extract the rate constants. To our knowledge, this method seems by far the most satisfactory one.

The measured rate constants were compared quantitatively with two parameter fitting laws. We found that the rate constants of $I_2^*-I_2$ and I_2^*-Ar scale according to the power-gap law which has been restricted in advance by the propensity rule $\Delta m_j = 0$, but the I_2^*-He system exhibits a new type of behavior and fits into a hybrid of power-gap and exponentialgap laws. These results are not in conflict with those of Dexheimer et al. A related result is the proof that $\Delta m_j = 0$ is valid in our collision-induced energy transfer experiment.

1. Experimental

The experimental set up is shown in Fig. 1, which consists essentially of a cw single-mode ring dye laser and an OMA-2 system (Optical Multichannel Analyzer). The instantaneous detection ability of the OMA system can effectively eliminate the fluorescence fluctuation over all the detection region. The fluctuation was due mostly to the instability of our dye laser. The polychromator of the OMA has been replaced by a 0.6 m monochromator with an entrance slit width of 10 μ m and with no outlet slit. In order to increase the spectral resolution, a f/2 aberrationless lens was placed behind the monochromator to further disperse

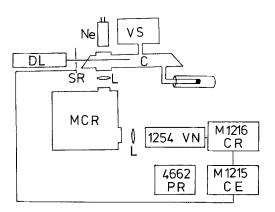


Fig. 1. A schematic diagram of the apparatus. (DL: dye laser; Ne: Ne hollow cathode lamp; VS: vacuum system; SR: light shutter; C: sample cell; MCR: monochromator; L: lens; VN: vidicon detector; CR: controller; CE: console; PR: plotter)

the fluorescence by a factor of 5, focusing on the vidicon target. Our achieved resolution was typically 0.65 cm^{-1} .

For the collision experiment of I_2^* -Ar and I_2^* -He, the I_2 vapor was produced in a glass cell connected to a vacuum system and evacuated to about 10^{-5} Torr. The sample gas was maintained at a number of pressures from 20 mTorr to 1 Torr and was measured with a capacitance membrane manometer while the iodine vapor was kept at a constant partial pressure of 30 mTorr corresponding to a constant temperature of 0° C. The study of I_2^* - I_2 was achieved by varying the temperature of the reservoir in which the iodine was bathed through a sidearm. The temperature in the reservoir was kept below that of the cell ($\simeq 25^\circ$ C) to avoid condensation on the cell wall.

Inelastic collision was investigated by measuring fluorescence intensities from the initial and the collisionally populated rotational levels as a function of collision gas pressure. Typically, 2–6 scans, depending on the fluorescence intensity, were taken at each pressure and averaged for a scanning time of 60 s.

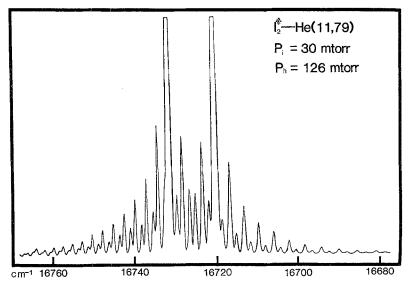
The laser was centered on a given rotational line by maximizing the signal from the Console(1215) screen. The fluorescence wavelengths were roughly assigned, at first, by the monochromator reading. Then we determined the exact values by use of a group of Ne atom lines to sandwich in between the fluorescence lines, and, furthermore, to coincide the fluorescence P/R doublet – the separation between the two parent lines – with the calculated P/R branch separation

The initial quantum number (v_0, j_0) was determined from the molecular constants published by Luc [7]. In fact, the splitting of the P/R branch lines can serve as a sensitive probe in ascertaining the line being excited.

As the molecules in the upper levels can fluoresce by jumping into different lower levels, there should be many sequences to appear on the screen as we tune the monochromator grating. We choose such a sequence that it had strong intensity but different wavelength from the initial sequence in order to eliminate the scattered laser light.

2. Data Reduction

A typical fluorescence spectrum is shown in Fig. 2. All spectra were first corrected for background and then for multiple-collision. The ultimate goal of our treatment for multiple-collision is to obtain the "real intensity ratio", i.e. the ratio for satellite line to parent line in the limit of zero pressure.



If the initial excited level is (v_0, j_0) , then the rate equation for the population N(j) of level (v_0, j) is given by

$$0 = \frac{dN(j)}{dt} = N(j_0)K(j_0 \to j) + \sum_{j'} N(j')K(j' \to j) - N(j)A(n_t, n_i) - \sum_{j'} N(j)K(j \to j')$$
(1)

with

$$K(i \rightarrow j) = n_t k_t(i \rightarrow j) + n_i k_i(i \rightarrow j), \qquad \sum_{j'} = \sum_{j' \neq j}, \qquad (2)$$

where $K(i \rightarrow j)$ represents the total rate per I_2 molecule in the level (v_0, i) at a given collision gas density n_i , and I_2 vapor density n_i for the rotational collision change $(v_0, i) \rightarrow (v_0, j)$; $k_t(i \rightarrow j)$ and $k_i(i \rightarrow j)$ are the corresponding rate constants. $A(n_i, n_i)$ denotes the total decay rate except rotational relaxation from level (v_0, j) at certain values of n_i and n_i . At present, we need not know the detail of $A(n_i, n_i)$.

With the notation of

$$T(i \rightarrow j, n_t, n_i) = K(i \rightarrow j) / A(n_t, n_i),$$

$$R(j', j) = N(j') / N(j),$$

Eq. (1) can be simply expressed as

$$1 = \sum_{j'} R(j', j) T(j \to j', n_t, n_i) - \sum_{j'} T(j' \to j, n_t, n_i).$$
(3)

In the above equation, R(j', j), the uncorrected population ratio, can be calculated from the measured quantity I(j) via

$$\frac{N(j)}{N(j_0)} = \frac{\nu_0^4(j_0)}{\nu^4(j)} \cdot \frac{S(j_0, j_0'')(2j+1)}{S(j, j'')(2j_0+1)} \cdot \frac{I(j)}{I(j_0)}$$
(4)

Fig. 2. Fluorescence spectrum of I_2^* -He collision with the laser pumping $v_0 = 11$, $j_0 = 79$

provided we know the Honl-London factors $S_j^R = j$ and $S_j^P = j + 1$ for the *R*-branch and *P*-branch, respectively, for the iodine $B^3\Pi_0^+$ state; $T(i \rightarrow j, n_t, n_i)$ represents the population ratio under the limit of zero pressure, $N(i)/N(j)|_{n_t \rightarrow 0, n_i \rightarrow 0}$. Now the question for multiple-collision correction reduces to how to calculate *T* from the experimentally measured quantity R(j', j) through (3).

As each satellite-line population N(j) needs a comb of other lines centered at j to correct for its value due to multiple-collision, we need to extend the N(j') value towards higher $|\Delta j| = |j' - j|$ when j is far from the parent line j_0 (we only measured experimentally for limited I(j) values, e.g. $[M^-, M^+]$). We first fitted N(j)by an exponential line and then extrapolated N(j).

Using the assumption that the rate of collisional transfer from (v_0, j_0) to $(v_0, j_0 + \Delta j)$ depends only on Δj (this assumption proved to be correct by our fitting law), T can be finally obtained from (3). This analysis is similar to that of Brunner et al. [5].

The $T(j_0 \rightarrow j, n_t, n_i)$ is insensitive for any reasonable extrapolation of N(j) within a j region of $[M^- - 4, M^+ + 4]$. This is due to the fact that the sum of rotational energy transfer rate constants for $j_0 \pm 2$ and $j_0 \pm 4$ accounts for about 65% of the total rotational energy transfer rate constants.

The preceding procedure has removed the effect of multiple-collisions between observed rotational levels and has thus led us to deduce k_i , k_i . From the definition of T, we have

$$T(j_0 \rightarrow j, n_t, n_i) A(n_t, n_i) = K(j_0 \rightarrow j, n_t, n_i)$$

= $n_t k_t (j_0 \rightarrow j) + n_i k_i (j_0 \rightarrow j)$ (5)

with

$$4(n_t, n_i) = 1/\tau' + n_t(k_{v,t}^Q + k_{e,t}^Q) + n_i(k_{v,i}^Q + k_{e,i}^Q),$$
(6)

where τ' is the effective lifetime. It includes the contributions from spontaneous lifetime, hyperfine predissociation and rotational predissociation. These terms are calculated using the results of Broyer et al. [3] and Tellinghuisen [8]; $k_{e,t}^Q$ and $k_{e,i}^Q$ are electronic decay rate constants for I^{*}₂ colliding with target gas and I²₂, respectively, and can be obtained from the data published by Broyer et al; $k_{e,t}^Q$ and $k_{e,t}^Q$ are for to

$$k_{v,t}^{Q} = a \sum_{j} k_{t}(j_{0} \rightarrow j) \tag{7}$$

vibrational decay rate constants and relate to the rate

with *a* being the efficiency ratio of vibrational to rotational energy transfers. For I_2^* -He and I_2^* -Ar, *a* is 0.7; for I_2^* - I_2 , *a* is 0.5 [9]. Combining (5, 6, and 7), we have an explicit expression

$$T(j_{0} \rightarrow j, n_{t}, n_{i}) \cdot \left\{ 1/\tau' + \left[a_{t} \sum_{j} k_{t}(j_{0} \rightarrow j) + k_{e,t}^{Q}(j_{0} \rightarrow j) \right] n_{t} + \left[a_{i} \sum_{j} k_{i}(j_{0} \rightarrow j) + k_{e,t}^{Q}(j_{0} \rightarrow j) \right] n_{i} \right\}$$
$$= n_{t}k_{t}(j_{0} \rightarrow j) + n_{i}k_{i}(j_{0} \rightarrow j) . \tag{8}$$

Equation (8) holds for each level j and represents a system of algebraic equations which are coupled by the Σ term. Since k_t and k_i contained in the Σ terms are just what we are seeking for, k_t has to be obtained from (8) using the following steps:

With the abbreviation

constant $k_t(j_0 \rightarrow j)$ via

$$\alpha = \tau \left[k_{e,t}^{Q} n_{t} + k_{e,t}^{Q} + a_{t} \sum_{j} k_{t} (j_{0} \rightarrow j) n_{t} + a_{t} \sum_{j} k_{i} (j \rightarrow j) n_{t} \right].$$
(9)

Equation (8) can be rearranged to

$$T \cdot 1/\tau'(1+\alpha) = n_t k_t + n_i k_i.$$
⁽¹⁰⁾

At low pressures $(<100 \text{ mTorr})\alpha \ll 1$ holds. Setting $\alpha = 0$, we obtain

$$T \cdot 1/\tau' = n_t k_t + n_i k_i \,. \tag{11}$$

In this case $k_t(j_0 \rightarrow j)$ and $k_i(j_0 \rightarrow j)$ can be obtained for all *j* directly from the fitting *T* vs. n_t . (In our experiment with I^{*}₂-He and I^{*}₂-Ar, n_i was kept constant at 30 mTorr.) Then we obtain $k_{v,t}^Q$ and $k_{v,i}^Q$ via (7) by taking the sum $\sum_j k_t(j_0 \rightarrow j)$ and $\sum_j k_i(j_0 \rightarrow j)$. In this way, we have initial values of $k_{v,t}^Q$ and $k_{v,i}^Q$ for (8) to perform an iteration approximation.

In our iterative method, each time the $k_t(j_0 \rightarrow j)$ and $k_i(j_0 \rightarrow j)$ were only obtained from least-squares fitting T in the expression (8) vs. n_t to get a better approximation of k_i and k_i and were used for the next iteration cycle. This process could be self-consistent for a few iteration cycle.

Table 1. Rate constants $k(j_0 \rightarrow j) [10^{-13} \text{ cm}^{-1}/\text{s}]$

∆j	$v_0 = 11, j_0 = 79$			$v_0 = 16, j_0 = 85$		$v_0 = 17, \\ j_0 = 95$
	I ₂ *–I ₂	I ₂ *-Ar	I ₂ -He	I ₂ *–I ₂	I [*] _He	J ₀ =95 I ₂ -He
-32			4			·
-30		12	5			
-28		14	6			
-26		16	9			
-24		20	13			
-22		22	18		16	
-20	17	27	24		22	15
-18	22	34	30	18	28	18
-16	26	38	35	25	37	22
-14	28	46	55	30	45	32
-12	41	52	64	37	48	40
-10	52	68	96	66	86	64
- 8	65	83	145	82	124	96
- 6	89	123	219	106	170	139
- 4	162	206	371	183	260	236
- 2	536	606	948	612	794	698
0						
2	448	495	859	561	761	574
4	131	159	281	154	235	167
6	120	144	146	75	175	118
8	79	96	93	53	140	71
10	36	43	51	41	58	44
12	29	39	33	33	45	27
14	21	29	27	24	28	18
16	17	21	17	21	16	17
18	12	15	13	16	13	14
20	7	13	9		10	13
. 22		10	7		7	
24		8	5			
26			3			
28			2			

All the calculated rate constants are listed in Table 1.

3. Discussion

That a selection rule $\Delta j = \pm 2n$ exists in the I₂ inelastic rotational energy transfer was first noted by Wood and Loomis [10]. Steinfeld gave an interpretation that based on an experimental result, nuclear spin states were not easily changed by collision [11]. Here we expound this phenomenon in a more rigorous way by virtue of the result of Alexander's theoretical investigation on inelastic collision.

The $I_2B^3\Pi_0^+$ state is a component of ${}^3\Pi$ state belonging to Hund's case (c), as we stated in Introduction. Its total parity of the eigenfunction $|JM\Omega v\varepsilon\rangle$ is $\varepsilon(-1)^{j-1}$. In line with current spectroscopic notations, the $\varepsilon = -1$ levels, with parity $(-1)^j$, are labeled *e*, and the $\varepsilon = +1$ levels, with parity $-(-1)^j$, are labeled *f*. Therefore, the selection rule $\Delta j = \pm 2n$ can be represented as $e \rightarrow e$ and $f \rightarrow f$ since the *e* levels appear

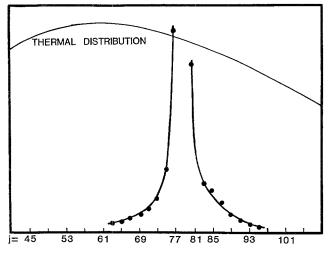


Fig. 3. Rate constants for $I_2^*-I_2$ collision plotted vs. *j* at $v_0 = 11$, $j_0 = 79$. The solid line is a thermal distribution for I_2 at 25°C

alternatively with the f levels. This result is in accordance with Alexander's conclusion that collisional change of the e/f symmetry index will be rigorously forbidden in the ${}^{3}\Pi_{0}$ manifold [12].

By inspection of the rate constants, a striking feature is their rapid trend of decrease with increasing $|\Delta j| = |j - j_0|$. In Fig. 3, we plotted the rate constants distribution vs. Δj and a thermal distribution for I_2 at the same temperature. It is plain that our observation is quite different from that predicted by a hard collision model which assume that the final *j* distribution will be similar to the thermal distribution for I_2 , shown as a solid line in Fig. 3, regardless of the initial *j*. (The quantitatively correct prediction of this model is the prior distribution of surprisal theory.) We conclude that our observed collisions are weak in the sense that many collisions are required to bring the system to thermal equilibrium.

Another apparent trend in the data is that the rates are asymmetric. The rate constants for $\Delta j < 0$ are larger than those for $\Delta j > 0$ with respect to j is conceivable. For the peak of the thermal distribution lies in $j_m \simeq 61$ and our data, listed in Table 1, have initial j_0 values greater than j_m . This asymmetry indicates a tendency to move towards equilibrium. We also examined our data for $j_0 = 41 < j_m$ (as the lines are too dense to be completely resolved, we did not list them in Table 1), the situation is just the opposite of those with $j_0 > j_m$.

Now we turn our attention to formulating a fitting law that best represents our rate constants.

An exponential-gap expression

$$k(j_0 \to j) \propto (2j+1) \left(T_f / T_i \right)^{1/2} \exp(-\vartheta |\Delta E|)$$
(12)

previously proposed for rotational energy transfer has been found, in the present study, to underestimate the rate constants for large rotational quantum jumps, as shown in Fig. 4a. Instead, the rate constants for $\Delta j < 0$ have been found to scale as an inverse power of the energy transfered in accordance with a recently proposed expression due to Brunner et al. [5]

$$k(j_0 \to j) \propto (2j+1) (T_f/T_i)^{1/2} |\Delta E|^{-\gamma},$$
(13)

where T_i and T_f are the initial and final relative translational energies, and ΔE is the energy gap between the initial and final levels. This expression is tested in Fig. 4b for the $I_2^*-I_2$ rate constants out of $(v_0 = 11, j_0 = 79)$. The linearity of the plot constitutes a test of (13).

When we used (13) to fit the rate constants with $\Delta j > 0$, the fitting line was slightly above most of the experimental data points for large $|\Delta j|$ although the result was much better than that predicted by the exponential-gap law (12). This phenomenon can be explained by the following discussion.

In the above fitting, we have assumed that there are no restrictions on the magnetic quantum numbers m_0 and m, i.e., a molecule in the initial state described by magnetic quantum number m_0 can jump into any final state m via collision. So the degenerate factor is 2j + 1, as shown in (13).

To date, the question that whether or not there exists a propensity rule $\Delta m_j = m - m_0 = 0$ in the energy transfer process is still unsettled. Evidences that Δm_j does not change drastically in rotational energy transfer were found in recent theoretical and experimental works [13] which suggested that m_j should be conserved, i.e., $\Delta m_j = 0$.

Application of this propensity rele to (13) only replaces 2j+1 by $(2j_{<}+1)/(2j_{0}+1)$, where $j_{<}$ is the smaller of j_{0} and j. Thus, for collisions in which jincreases, $(2j_{<}+1)/(2j_{0}+1)=1$; while for $j < j_{0}$, we have $(2j+1)/(2j_{0}+1)$. This means that the restriction $\Delta m_{j}=0$ does not change the fitting law (13) at all for $\Delta j < 0$ and only slightly for $\Delta j > 0$.

By using the fitting law

$$k(j_0 \to j) \propto \frac{2j_{<} + 1}{2j_0 + 1} (T_f / T_i)^{1/2} \cdot |\Delta E|^{-\gamma}$$
(14)

to fit the rate constants for $I_2^*-I_2$ and I_2^*-Ar , we obtain satisfactory results, one of which is shown in Fig. 4c.

When we turned to the rate constants for I_2^* -He, it was obvious that a power law could not adequately describe the extremely rapid decrease of the I_2^* -He rate constants at large $|\Delta j|$. This phenomenon is similar to that observed by Dexheimer. We propose a simple energy-based law, which is a hybrid between a power gap law and an exponential gap law,

$$k(j_0 \rightarrow j) \propto \frac{2j_{<} + 1}{2j_0 + 1} (T_f/T_i)^{1/2} \cdot \exp(-\vartheta |\Delta E|) \cdot |\Delta E|^{-\gamma}$$
(15)

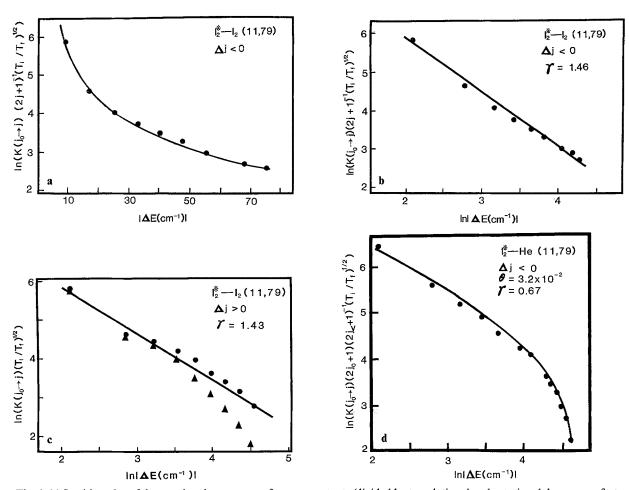


Fig. 4. (a) Semi-log plot of the rotational energy transfer rate constants (divided by translational and rotational degeneracy factors) vs. $|\Delta E|$. This is equivalent to a surprisal plot and would be a straight line if the exponential-gap law holds. The curved line represents the failure of exponential-gap law and suggests the use of a power-gap fitting law. (b) Log-log plot of $k(j_0 \rightarrow j)/(2j+1)$ $(T_f/T_i)^{1/2}$ vs. $|\Delta E|$. The straight line establishes the success of the power gap law, see (13). (c) Log-log plot of $k(j_0 \rightarrow j)/(2j+1)$ $(T_f/T_i)^{1/2}$, marked with •, and $k(j_0 \rightarrow j)/(2j+1)$ $(T_f/T_i)^{1/2}$, marked with \blacktriangle , vs. $|\Delta E|$. That these darked circle points (•) are well fitted by a straight line even for large $|\Delta E|$ in contrast to the curvature of the darked triangles (\bigstar) shows that there exists a propensity rule, $\Delta m_j = 0$, in $I_2^*-I_2$ inelastic collision. (d) Log-log plot of $k(j_0 \rightarrow j)/(2j+1)/(2j_0+1)]$ $(T_f/T_i)^{1/2} = a - \vartheta |\Delta E| - \gamma \ln(|\Delta E|)$ vs. $|\Delta E|$. The rate constants of I_2^* -He collision are quite well fitted by the hybrid law shown by the solid line, see (14)

to fit our data with a computer, using a nonlinear program. The results are satisfactory, as partly shown in Fig. 4d.

4. Conclusion

In conclusion, we would like to remark that fitting laws are just one way of describing the rate constants. They should portray rate constants with the least number of parameters. Both the exponential-gap law and the power-gap law are successfully applied to most of the previous experimental data, including those for $I_2^*-I_2$ and I_2^* -Ar systems, with only one parameter ϑ or γ . But sometimes, as in our I_2^* -He collision, the data behaves as an intermediate case and only the prescribed hybrid law is valid. Furthermore, our hybrid law can be

Table 2a.	Power-law	coefficients

Coeff.	$v_0 = 11, j_0 = 79$ $I_2^* - I_2$		0 , 20		$v_0 = 16, j_0 = 85$ $I_2^* - I_2$	
	j<0	j>0	j<0	j>0	j<0	j>0
γ	1.46	1.43	1.38	1.43	1.57	1.42

Table 2b.	Exponential-power	(hybrid) la	w coefficients
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Coeff.	$v_0 = 11, j_0 = 79$		$v_0 = 16, j_0 = 85$		$v_0 = 17, j_0 = 95$	
	I ₂ *-He		I ₂ -He		I ₂ -He	
	j<0	j>0	j<0	j>0	j<0	j > 0
$\frac{\gamma}{9}$	0.67	1.13	1.14	0.89	1.21	1.56
(×10 ⁻²)	3.2	1.74	1.32	1.97	1.41	1.49

readily reduced into the two extreme cases, viz., exponential law and power law, when γ or ϑ becomes very small compare to the other parameter. So we suggest that this hybrid exponential-power gap law should work as a fitting law widely applicable to a whole range of collision-induced energy transfer processes. We tend to believe that our data, together with the observed propensity rule of m_j conservation, could serve as a stimulus to further theoretical studies.

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