

ANALYSIS OF ELECTRONICALLY NONADIABATIC CHEMICAL REACTIONS: AN INFORMATION THEORETIC APPROACH*

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A practical procedure for the determination of branching ratios for reactions which lead to either excited or electronically ground state products is outlined. The method is applied to four reactions which could (on energetic grounds) produce an electronically excited iodine atom. No case of a complete inversion is found, but one reaction ($F + HI$) is predicted to yield a statistical, (one half), $I^*(^2P_{1/2})$ to $I(^2P_{3/2})$ ratio.

1. Introduction

There are two major reasons why the formation of electronically excited products in chemical reactions [1] is of current interest. On the practical side such reactions could provide the pumping mechanism for chemical laser action in the visible and near UV spectral regions. From the theoretical point of view these processes shed light on the degree to which chemical reactions proceed on a single electronic energy surface (i.e., are electronically adiabatic). While the problem is receiving considerable current theoretical attention [2–10], it has not yet reached a fully predictive state.

In this letter we consider an alternative approach using the information theoretic procedure for the determination of branching ratios [11]. For simplicity the discussion is limited to an $A + BC$ type reaction. We show that (except for the structural factor [12])

the prior expectation for the magnitude of the branching ratio (excited versus ground state reaction products), is of the form $[(E - \Delta E)/E]^{5/2}$. E is the total energy available for the reaction products and ΔE is the electronic excitation energy. Hence the prior branching ratio always favors the formation of the electronically ground state products. In particular, at energies not much above the threshold for formation of excited products (i.e., for E just above ΔE), they are strongly disfavored on prior grounds. (Thus, even when $E = 2\Delta E$ the ratio above is 0.177.) Since electronic excitation energies are usually above 1 eV and since few chemical reactions have exoergicities in excess of 2 eV, the prior prognosis is not favorable.

In the absence of any information the most reasonable (i.e., least presumptive) assumption is that the branching ratio equals its prior expectation. Often however we do have some additional information. In particular, molecular beam, chemiluminescence, and chemical laser techniques [1] provide information on the translational or the vibrotational (or vibrational) energy disposal in the products. In this letter we show how such information can be used to predict the electronic

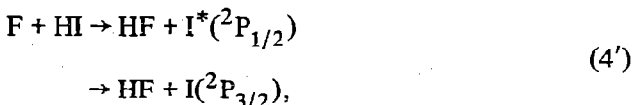
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branching ratio and how the prediction can be checked for self-consistency. We apply the method to the existing experimental data for the following reactions:



In all cases the exoergicity of the reaction suffices to form an electronically excited [$\text{I}^*(^2\text{P}_{1/2})$, $\Delta E = 7603 \text{ cm}^{-1}$] iodine atom. Thus, e.g., reaction (4) is to be written as



and similarly for the other reactions. Our conclusion is that, with the exception of the $\text{D} + \text{I}_2$ reaction, there is significant formation of electronically excited iodine atoms. The branching ratio, Γ , for all reactions does not suffice however for electronic chemical laser action which requires $\Gamma > 0.5$. The most efficient in this respect is reaction (4) for which[†] $\Gamma = 0.5$.

2. The theoretical approach

We outline the theory in three steps. We first define our prior expectations [12]. Then we note the general expression [11] for the deviation of the actual branching ratio from its prior value. Finally, we specialize the general expression to the form actually employed in the analysis.

Let p_a^0 be the prior expectation for the branching fraction, i.e., p_a^0 is the fraction of all reactive collisions that we expect, in the absence of any information, to lead to products of type a . $\Gamma_{ab}^0 = p_a^0/p_b^0$ is the prior ex-

pectation for the branching ratio for products of type a versus type b . Our prior expectations are [13–16] that, at a given energy and in the absence of additional information all product quantum states are equally probable (i.e., are formed with the same rate). This assumption can be shown [12,16] to imply that

$$\Gamma_{ab}^0 = \rho_a(E_a)/\rho_b(E_b). \quad (5)$$

Here $\rho_a(E_a)$ is the total density of quantum states of products of type a at the available energy E_a and similarly for type b . Using the RRHO level scheme [14] one shows that $\rho_a(E_a) = A_a E_a^{5/2}$. Here A_a is a (unit-bearing) factor. When one considers branching into two different electronic states of the same chemical type products, the mass dependence of the structural factor A_a/A_b cancels. Hence for this case, in the RRHO limit,

$$\Gamma_{ab}^0 = (g_a/g_b) [(\omega_e B_e)_b / (\omega_e B_e)_a] (E_a/E_b)^{5/2}. \quad (6)$$

Here g_a and g_b are the electronic degeneracies of the two states. ω_e and B_e are the vibrational frequency and rotational constant respectively. The subscripts a and b refer to the two different electronic states. $\Delta E = E_b - E_a$ is the difference in electronic excitation energy.

For reactions (1)–(4), the diatomic molecule is in the ground electronic state for both reaction paths. Hence the middle factor in (6) is unity, the structural factor is just $A_a/A_b = g_a/g_b$ and

$$\Gamma_{ab}^0 = (g_a/g_b) (E_a/E_b)^{5/2}. \quad (7)$$

For the iodine atom, taking a to be the excited ($^2\text{P}_{1/2}$) state, $g_a/g_b = 1/2$.

Thus far we have considered the prior expectations. The general theory of branching ratios [11,12,16] provides the following expression for the actual branching fraction, p_a ,

$$\ln(p_a/p_a^0) + \Delta S_a/R = \alpha(a). \quad (8)$$

Here ΔS_a is the entropy deficiency [14] for the products of type a . $\alpha(a)$ is a Lagrange multiplier which, in the absence of information to the contrary, is to be taken as a constant (i.e., independent of the type of the products). In that case, α is just the lagrangian multiplier that ensures that p_a is normalized. Thus α is determined by

$$\exp(-\alpha) = \sum_a p_a^0 \exp(-\Delta S_a/R). \quad (9)$$

[†] At the risk of stating the obvious, we point out that our branching ratios are only as accurate as the experimental data used in the analysis. Improvements in arresting the relaxation in chemiluminescence experiments could thus change somewhat our conclusions for reaction (4). For reactions (1) through (3) (which derive from molecular-beam data), improved lab to c.m. conversion could slightly affect our results.

When α is taken as a constant we obtain from (8) for $\Gamma_{ab} = p_a/p_b$

$$\Gamma_{ab} = \Gamma_{ab}^0 \exp[-(\Delta S_a - \Delta S_b)/R]. \quad (10)$$

We shall use this equation with the entropy deficiencies computed using molecular beam [17–19] or chemiluminescence [20] data to predict the, as yet unmeasured, electronic branching ratio.

3. The synthetic analysis of experimental results

The following information is currently available to us from experiment. For reactions (1)–(3) there are molecular beam measurements [17–19] of the translational energy disposal, $\mathcal{P}(f_T)$, of the products[†]. For reaction (4) there are chemiluminescence data [20] of the vibrational state distribution of HF. To analyze both types of data we have adopted the so-called [16] synthetic route, as follows. We have assumed that each vibrotational state of the product diatomic could be accompanied by either ground or excited iodine atom, subject to conservation of total energy. We have then assigned to each state its “information theoretic” weight, using a linear vibrotational surprisal [14,16] (for each product type separately). Explicitly, if $P^*(f_v, f_R)$ is the distribution of the vibrotational states of the diatomic molecule which is formed together with an excited iodine atom then

$$P^*(f_v, f_R) = P^{0*}(f_v, f_R) \exp(-\lambda_v^* f_v) \exp[-\theta_R^* f_R / (q^* - f_v)] / Q^*. \quad (11)$$

Here P^{0*} is the prior expectation distribution [14,16]

$$P^{0*}(f_v, f_R) = \frac{1}{4}(q^*)^{-5/2} (q^*)^{-5/2} (q^* - f_v - f_R)^{1/2}. \quad (12)$$

Q^* ensures that $P^*(f_v, f_R)$ is normalized. f_v and f_R are, as usual, the fraction of the total energy in the vibration and rotation respectively. Hence, the range of f_v is 0 to q^* ,

$$q^* = E^*/E = (E - \Delta E)/E \quad (13)$$

and the range of f_R (for a given value of f_v) is 0 to

$$q^* - f_v.$$

The distribution of the diatomic vibrotational states when a ground state iodine atom is formed, $P(f_v, f_R)$, has a form identical to (11) except, of course, that $q = 1$.

The actual (observed) vibrotational state distribution of the diatomic molecule, irrespective of the electronic state of the iodine atom is then of the form

$$\mathcal{P}(f_v, f_R) = pP(f_v, f_R) + p^*P^*(f_v, f_R). \quad (14)$$

Here p and p^* are the branching fractions for formation of ground and excited iodine atoms respectively. The branching ratio as determined by the synthesis is

$$\Gamma = p^*/p. \quad (15)$$

For the purpose of analyzing reactions (1)–(3) the vibrotational state distribution was converted to a translational energy distribution. Since

$$f_T = 1 - f_v - f_R \quad (16)$$

one can readily convert $\mathcal{P}(f_v, f_R)$ to $\mathcal{P}(f_T)$. Explicitly one sums $\mathcal{P}(f_v, f_R)$ over all values of f_v and f_R that correspond, according to (16), to a given value of f_T . In practice this is carried out by replacing [in (14)] f_R by $1 - f_v - f_T$ and then integrating over the allowed range of f_v (i.e., 0 to $q^* - f_T$ or 0 to $1 - f_T$, depending on the path). In a similar fashion, say, $P^*(f_v, f_R)$ can be converted to $P^*(f_T)$. Thus we can rewrite (14) as

$$\mathcal{P}(f_T) = pP(f_T) + p^*P^*(f_T), \quad (14')$$

where, as usual, $p + p^* = 1$, and both $P(f_T)$ and $P^*(f_T)$ are normalized.

Eq. (14) contains five ($\lambda_v, \lambda_v^*, \theta_R, \theta_R^*, p^*/p$) unknown parameters. Since experimental product translational or internal energy distributions for reactions (1)–(4) are not highly-structured, we might question whether a unique five-parameter fit can be found. Fortunately, thermochemical and other constraints can be applied in order to restrict the range of plausible fitting parameters.

A strong constraint is provided by system thermochemistry – at $f_T > q^*$ or $f_v > q^*$, only the ground state iodine atom channel [$I(^2P_{3/2})$] is energetically open. Thus, the ground state component fit must match the high recoil translational energy ($f_T > q^*$) portion of product distributions for reactions (1)–(3) and the high vibronic energy ($f_v > q^*$) portion of the product

[†] For reaction (2), the product angular distribution (the primary measurement) was used to deduce the product translational energy distribution [18].

distribution for reaction (4).

In principle, another strong constraint is provided by the general theory of branching ratios [11,12,16] which results in eq. (10) above. In practice, our lack of knowledge about detailed product angular and polarization distributions (which contribute to the total entropy deficiency of each product channel) forces us to proceed cautiously with the application of eq. (10) as a consistency check or as a predictive tool.

Intercomparisons of reactions (1)–(4) with related reaction examples guide our choice of parameters; for example, available experimental data indicate that product rotational state distributions do not deviate markedly from the prior, non-surprising ($\theta_R \approx 0$) expectations [21,22].

4. Results

4.1. $K + I_2$ reaction

Fig. 1 shows a synthetic analysis of the $KI + I$ recoil translational energy distribution matched to the experimental results [17]. A thermochemical constraint requires that $KI + I(^2P_{3/2})$ products are solely responsible for the high-energy tail of the distribution [i.e., for $f_T > q^* (= 0.51)$]; this constraint leads to a family of suprisal fitting parameters [λ_v, θ_R in the analogue of eq. (11)], but a nearly constant branching ratio: $\Gamma = 0.26$ – 0.30 , independent of the member of the λ_v, θ_R family. A fit to the "experimental" $KI + I(^2P_{1/2})$ product recoil translational energy distribution [determined by subtraction of the synthesized $KI + I(^2P_{3/2})$ distribution from the complete experimental distribution] can also be made using members of a large family of λ_v^*, θ_R^* surprisal fitting parameters.

Two prior expectation distributions were used: (i) the RRHO (rigid rotator harmonic oscillator) level density [14] and (ii) the exact level density of KI computed from its rovibronic state spectrum as described in the appendix. For $P_{\text{exact}}^0(f_T)$, the best fit (shown in fig. 1) was obtained for non-surprising (i.e., statistical) rotational parameters: $\theta_R = \theta_R^* = 0$ and highly-surprising vibrational parameters: $\lambda_v = -3.3$ and $\lambda_v^* = -24$. A slightly worse fit was obtained using $P_{\text{exact}}^0(f_T)$ with the opposite extremes of surprisal constants: non-surprising vibrational parameters ($\lambda_v = \lambda_v^*$

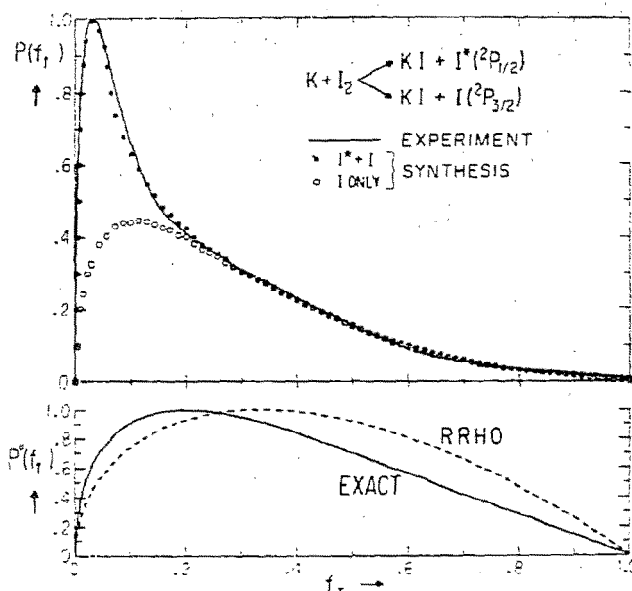


Fig. 1. Top panel: experimental [17] and synthesized translational energy disposal for the $K + I_2$ reaction. Branching ratio fitting parameters (cf. table 1) were determined using $P_{\text{exact}}^0(f_T)$ for the prior expectation distribution. Although I^* can be formed at $f_T \leq 0.51$, the synthesized I^* distribution makes little contribution beyond $f_T = 0.30$. Bottom panel: exact (cf. appendix) and RRHO prior expectation distributions.

$= 0$) and highly-surprising rotational parameters ($\theta_R = -2$, $\theta_R^* = -8$). An adequate fit was also obtained using $P_{\text{RRHO}}^0(f_T)$, but larger surprisal constants were required (e.g., for $\theta_R = \theta_R^* = 0$, $\lambda_v = -4.5$, $\lambda_v^* = -25$) since $P_{\text{RRHO}}^0(f_T)$ incorrectly favors higher recoil translational energy (cf. fig. 1, bottom panel).

The prediction of the branching ratio for I^* versus I production ($\Gamma = 0.26$ – 0.30) derived from the synthetic analysis may, in principle, be tested for self-consistency with the general branching relation [eq. (10)]. In the absence of complete entropy deficiency data for each channel, we assume that the major contribution to the entropy deficiency is the energy disposal part:

$$\Gamma = \Gamma^0 \exp \{ -(\Delta S^*[T] - \Delta S[T])/R \}. \quad (17)$$

Here $\Delta S^*[T]$ is the entropy deficiency of the translational energy distribution when $I^*(^2P_{1/2})$ is formed^{††},

$$\Delta S^*[T] = R \int df_T P^*(f_T) \ln [P^*(f_T)/P^0(f_T)], \quad (18)$$

^{††} Footnote see next page.

and similarly for $\Delta S[T]$. The distributions employed are those generated in obtaining a synthetic fit to the experimental data.

The branching ratios obtained from eq. (17) ($\Gamma = 0.03-0.04$ for various $\theta_R, \theta_R^*, \lambda_v, \lambda_v^*$ parameters) are in poor accord with the synthetic values, suggesting that larger entropy deficiencies due to angular and polarization contributions are associated with the $KI + I(^2P_{3/2})$ than with the $KI + I(^2P_{1/2})$ products.

4.2. $F + I_2$ reaction

Reasonable synthetic fits to the experimental $FI + I$ recoil translational energy distribution [18] were obtained for a wide variety of $\lambda_v, \lambda_v^*, \theta_R, \theta_R^*$ fitting parameters. Fig. 2 shows the fit (summarized in table 1) for which the synthetic branching ratio closely corresponds to the branching ratio calculated from eq. (17).

The apparent self-consistency between synthetic analysis and general branching theory analysis [using eq. (17), an approximation to eq. (10)] cannot, however, be claimed as a major success. The shape of the $FI + I$ recoil energy distribution is not known accurately from experiment^{††}; hence, a stringent test of the match between the synthetic fit and the experimental data cannot be made.

4.3. $D + I_2$ reaction

In contrast to $K + I_2$ and $F + I_2$ reaction examples (for which significant yields of excited iodine atoms are predicted), a synthetic fit to the experimental $DI + I$ recoil translational energy distribution [19] can be made without invoking $I^*(^2P_{1/2})$ formation.

^{††} The mathematically inclined reader might worry that while (17) was proved [11] for a discrete distribution we are actually using a continuous one. This turns out to be not an idle worry. However, when several misleading statements in the information-theoretic literature are corrected, one can provide a proof for the continuous case as well [23].

[†] Wong and Lee [18] used an assumed (generalized RRR) functional form for the (uncoupled velocity-angle) recoil translational energy distribution: $P(f_T) = f_T(1 - f_T)^5$. The average translational energy should be well characterized by this procedure, but the detailed shape of the distribution is unknown (cf. fig. 6 and discussion in ref. [24]).

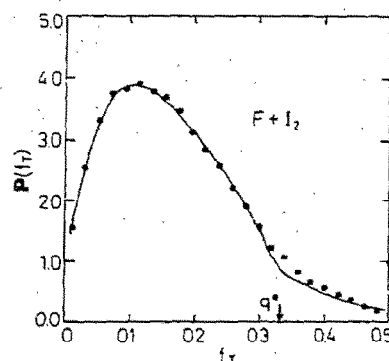


Fig. 2. Experimental [18] (points) and synthesized (curve) translational energy disposal for the $F + I_2$ reaction. $P_{RRHO}^0(f_T)$ was used as the prior expectation distribution in order to calculate branching parameters (collected in table 1).

4.4 $F + HI$ reaction

Infrared chemiluminescence measurements [20] of the HF product vibronic state distribution resulting from the $F + HI$ reaction can be analyzed by using a thermochemical constraint. The strongly populated $v = 5$ and 6 states can be formed only when accompanied by a ground state iodine atom. Thus λ_v can be readily determined from [14]:

$$P(f_v) = P^0(f_v) \exp(-\lambda_v f_v) / Q. \quad (19)$$

Having determined λ_v one can predict the populations of HF in $v < 5$ states formed together with ground state iodine atoms. These, together with the experimental results for $v < 5$ are then used to determine λ_v^* .

Table 1
Measures of specificity of energy disposal

Data	$K + I_2$ [17]	$F + I_2$ [18]	$F + HI$ [20]
$E(\text{kcal/mole})$	44.5	32.1	66
$E^*(\text{kcal/mole})$	22.8	10.4	44.3
λ_v	-3.3	-10.8	-7.7
λ_v^*	-24	-1.4	-3.2
θ_R	0	3.8	-
θ_R^*	0	3.8	-
Γ^B	0.09	0.03	0.18
Γ , eq. (17)	0.03	0.30	-
Γ , eq. (21)	-	-	0.7
Γ , eq. (15)	0.30	0.24	0.5

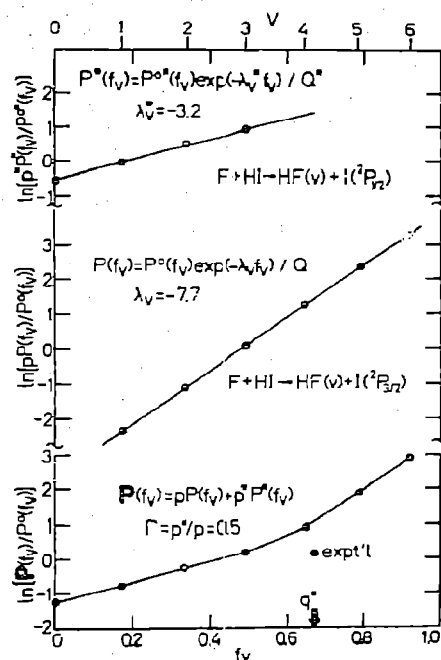


Fig. 3. Synthesis of the F + HI vibrational energy disposal (• experimental [20] points). The curves connect the synthesized points. Bottom panel: a surprisal analysis [14] of the experimental data using $P^0(f_v)$ appropriate for the formation of $I(^2P_{3/2})$ exclusively. The plot is non linear. From the points at $v = 5$ and 6 , λ_v can be determined. The values of $pP(f_v)$ for other values of v can then be read from the graph in the mid-panel (open circles). Using these values the graph in the top panel is constructed, and λ_v^* can then be determined. One can now synthesize the entire experimental distribution, as shown in the bottom panel. [Note that $P^0(f_v) = \frac{5}{2}(1 - f_v)^{3/2}$ and $P^{0*}(f_v) = \frac{5}{2}(q^* - f_v)^{3/2}/q^{*5/2}$, p and p^* are determined by the condition that both $P(f_v)$ and $P^*(f_v)$ are (separately) normalized to unity.]

The validity of this synthetic fit is evident in fig. 3. The synthetically determined branching ratio is thus free of ambiguities and is of the same quality as the experimental results themselves. This reaction could thus serve as an excellent test of the theory. Unfortunately, we do not yet know the complete rovibronic state distribution (together with the angular and polarization distributions) which would be necessary to provide an accurate estimate of ΔS and hence of Γ . In the absence of this detailed data we adopt the following (optimal) procedure. In the absence of information to the contrary we must assume that all (energetically accessible) rotational states (of a given vibrational manifold) are equally probable. This corresponds to taking $\theta_R^* =$

0 in eq. (11) and similarly for θ_R . In this case one can readily show that the entire entropy deficiency is determined by the vibrational energy disposal, e.g.,

$$\Delta S^*[v] = R \sum_v P^*(v) \ln[P^*(v)/P^{0*}(v)], \quad (20)$$

and similarly for $\Delta S[v]$. Hence, we determine Γ from

$$\Gamma = \Gamma^0 \exp \{ -(\Delta S^*[v] - \Delta S[v])/R \}. \quad (21)$$

This procedure yields 0.7 as opposed to the synthetic value of 0.5.

5. Discussion

Our analysis suggests that highly exoergic chemical reactions can produce significant fractions of electronically excited products. Moreover, by examining the explicit expression [eq. (6)] for the prior branching ratio one can devise ways of tilting the balance in favor of excited products (e.g., higher $E/\Delta E$, use of reactions where the diatomic molecule carries the electronic excitation, etc.). Although predicted yields of $I^*(^2P_{1/2})$ are substantially higher than the prior expectations, the actual branching ratios reported in table 1 are insufficient for lasing action.

The predictions we have made are not definitive; further (direct) experimental measurements of the branching ratios are required in order to elucidate the dynamics of electronically nonadiabatic processes on multiple potential hypersurfaces[†]. It is our opinion that the F + HI reaction is highly suitable for detailed experimental studies by infrared chemiluminescence [using arrested relaxation methods to prevent the facile energy transfer between $I^*(^2P_{1/2})$ and HF (cf. appendix A of ref. [25])], molecular beam reactive scattering, and chemical laser techniques.

Branching ratio parameters (λ_v , λ_v^* , θ_R , θ_R^* , Γ) determined by our syntheses reveal essential dynamical

[†] For simplicity, we have treated the $A + BI \rightarrow AB + I$ reactions as two-channel problems. In fact, only half of the $I(^2P_{3/2}) + AB$ products correlate to the ground potential hypersurface (X^2A' in C_s symmetry) of the ABI system; the other half correlate to an excited hypersurface ($^2A''$). $AB + I^*(^2P_{1/2})$ products correlate to an excited $^2A'$ hypersurface of the ABI system. A full dynamical treatment of the electronic nonadiabaticity may therefore require consideration of at least three separate hypersurfaces.

information about electronically nonadiabatic reactive processes. For example, it is tempting to speculate that a restricted range of impact parameters and other initial conditions gives rise to the extraordinarily surprising $\text{KI} + \text{I}^*(^2\text{P}_{1/2})$ product recoil energy distribution; this restricted range of initial conditions may be required for efficient hypersurface crossing to the excited $^2\text{A}'$ surface which correlates to $\text{KI} + \text{I}^*(^2\text{P}_{1/2})$ products. Further refinements of branching ratio theory and applications will certainly provide valuable diagnostic tools for dynamical understanding of reactive encounters.

Acknowledgement

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Appendix

The RRHO level density scheme is an inadequate representation for KI level densities over the entire range ($\leq 16000 \text{ cm}^{-1}$) accessible in the $\text{K} + \text{I}_2$ reaction. Therefore, an exact level density was calculated by using the complete spectrum of KI rovibronic states determined from the effective potentials ($J \leq 550$):

$$V_{\text{eff}}(R) = V_{[2,2]\text{PA}}(R) + \hbar^2 J(J+1)/2\mu R^2 \quad (22)$$

by the JWKB quantization condition [26]:

$$(v + \frac{1}{2})_J = (\pi\hbar)^{-1} \int_{R_{\min}}^{R_{\max}} \{2\mu[E_{v,J} - V_{\text{eff}}(R)]\}^{1/2} dR. \quad (23)$$

In eqs. (22) and (23), the rotationless potential $V_{[2,2]\text{PA}}(R)$ is the [2,2] Padé approximant [27], v, J are the vibrational, rotational quantum numbers, and $R_{\min}, R_{\max}$ are the inner, outer classical turning points.

The bottom panel of fig. 1 shows the difference between exact and RRHO prior expectation distributions for KI at $E_{\text{internal}} \leq 16000 \text{ cm}^{-1}$ [corresponding to $\text{KI} + \text{I}(^2\text{P}_{3/2})$ products], the deviation between $P_{\text{exact}}^0(f_T)$ and $P_{\text{RRHO}}^0(f_T)$ for the $\text{KI} + \text{I}^*(^2\text{P}_{1/2})$ channel is less pronounced.

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