

Validity of energy gap representations of rotationally inelastic cross sections between polar molecules

Millard H. Alexander, Eugene F. Jendrek, and Paul J. Dagdigan

Citation: *The Journal of Chemical Physics* **73**, 3797 (1980); doi: 10.1063/1.440609

View online: <http://dx.doi.org/10.1063/1.440609>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/73/8?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[The interaction of He with vibrating HCN: Potential energy surface, bound states, and rotationally inelastic cross sections](#)

J. Chem. Phys. **139**, 034304 (2013); 10.1063/1.4813125

[Statistical inelastic crosssection model for the Monte Carlo simulation of molecules with continuous internal energy](#)

Phys. Fluids A **5**, 778 (1993); 10.1063/1.858664

[Stateresolved rotationally inelastic cross sections of CaCl \(\$X\ 2\Sigma^+\$ \) with polar molecule targets](#)

J. Chem. Phys. **82**, 1341 (1985); 10.1063/1.448457

[Dynamical thresholds and quantum undulations in the energy dependence of rotationally inelastic integral cross sections](#)

J. Chem. Phys. **75**, 5449 (1981); 10.1063/1.441946

[Energy transfer processes in monochromatically excited iodine. IX. Classical trajectory and semiclassical calculations of vibrationally and rotationally inelastic cross sections](#)

J. Chem. Phys. **60**, 3082 (1974); 10.1063/1.1681494



Validity of energy gap representations of rotationally inelastic cross sections between polar molecules

Millard H. Alexander and Eugene F. Jendrek^{a)}

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Paul J. Dagdigan^{b)}

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

(Received 14 May 1980; accepted 1 July 1980)

In a collaborative investigation of rotational energy transfer between polar molecules, we have reported experimental state-resolved cross sections for LiH($j = 1$)-HCl, DCl, HCN collisions [J. Chem. Phys. **71**, 1670 (1979); **72**, 6513 (1980)] and fully quantum cross sections for HF-HF collisions [J. Chem. Phys. **66**, 1334 (1977) and to be published]. In the present article we apply both the exponential gap (EG) and power law (PL) parameterizations to the results of our experimental and theoretical study. Neither of these parameterizations is able to fit with high accuracy the HF-HF cross sections. Furthermore, this comparison reveals an inaccuracy in the statistical "prior" distribution which cannot be corrected by any multiplicative factor dependent on the energy gap. The fits were not greatly improved by the use of an alternative tensorial prior, suggested by group theoretic rather than statistical considerations. For the LiH scattering systems, the experimental cross sections can be fit extremely well by a power law dependence on the energy gap of the resolved LiH molecule. Unfortunately, it is improbable that either the PL or the EG fits to these partially averaged cross sections could be used to predict with any degree of accuracy the more fundamental fully resolved cross sections, as revealed by comparison with recently computed adiabatically corrected sudden cross sections [J. Chem. Phys. **71**, 1683 (1979)].

I. INTRODUCTION

Lately there has been much interest in the development of simple models for rotational energy transfer in molecular collisions. The most widely adopted of these grew out of the original suggestion by Polanyi and Woodall¹ that rate constants for rotational energy transfer might vary inversely with the change in rotational energy of the system. This "exponential gap" model was subsequently used by Polanyi and co-workers to interpret both experiments^{2,3} and theoretical calculations^{4,5} and has been given additional justification by the extensive information theoretic formalism of molecular collision processes developed by Levine, Bernstein, and collaborators.^{6,7} This latter work led to the "linear surprisal" model, wherein the deviation of $R - T$, R cross sections from a purely statistical prediction is represented by an exponential dependence on the rotational energy gap. Support for the linear surprisal model was provided by a detailed analysis of available experimental and theoretical data^{8,9} and by subsequent justifications of the functional form by formal treatments of the inelastic collision dynamics.¹⁰⁻¹² All this work has encouraged the recent use of these exponential gap models in the simulation of the time evolution of nonequilibrium gas phase systems¹³⁻¹⁷ and in the interpretation of rotational relaxation experiments.¹⁸⁻²⁰

Some recent results, both experimental²¹⁻²⁴ and theoretical,^{4,9,24-27} now indicate that at least in certain cases the linear surprisal model may be overly sim-

plistic, since the appropriate surprisal plots display pronounced curvature or scatter. Although curvature could be reproduced by the incorporation of additional dynamical constraints into the exponential functionality,²⁸ Pritchard and co-workers²²⁻²⁴ have suggested that a power law rather than exponential dependence on the energy gap provides a substantially better representation.

Although some methods have been presented for the direct prediction of the appropriate parameters,^{7,10-12,29} in general accurate values can only be obtained by a fit to either experimental data or the results of theoretical calculations. Nonetheless, it has often been argued^{6-8,10-13} that the parameters of the fit, albeit *a posteriori*, do have significant physical content and can consequently be used to compare various collision systems and to extrapolate to conditions different from those which characterized the fitted data.

Recently, we have been engaged in a collaborative experimental^{30,31} and theoretical³²⁻³⁴ study of rotationally inelastic collisions between polar molecules. This has involved the measurement of state-resolved cross sections for the collision of LiH ($j = 1$) with HCl, DCl, and HCN target gases,^{30,31} the development of the computationally rapid yet reasonably accurate adiabatically corrected sudden (ACS) approximation for the description of these experiments,³² and the determination of fully quantum cross sections for the prototype HF-HF system.^{33,34}

In the present article we shall use the results of this joint study to assess the validity and applicability of the two energy gap models (exponential and power law) to rotational energy transfer between polar molecules. We shall attempt to answer the following questions: Can these models provide an accurate representation of partially averaged relaxation data; do the parameters so ob-

^{a)} Work performed by E. F. Jendrek in partial fulfillment of the requirements for the degree of Ph.D. in Chemistry at the University of Maryland, College Park. Present address: Monsanto Research Corporation, Miamisburg, OH 45342.

^{b)} Alfred P. Sloan Research Fellow; Camille and Henry Dreyfus Teacher-Scholar.

tained provide a means to predict accurately more highly resolved cross sections; and, finally, are these models sufficiently flexible to provide a satisfactory fit to accurate, theoretically determined $j_a j_b \rightarrow j'_a j'_b$ cross sections? Three earlier articles make the present careful assessment particularly relevant. The first two are the papers by Sathyamurthy and Polanyi,⁵ and Turfa and Marcus³⁵ where the exponential gap model was used to fit the results of two distinct classical trajectory studies of rotational energy transfer in the HCl-HCl system. The third relevant article is the formal justification by Alhassid and Levine¹¹ of the linear surprisal model. One of the two examples used by these authors was the impact parameter sudden treatment³⁶ of rotationally inelastic collision between two polar molecules.

The energy gap models, briefly reviewed in the next section, are then applied in Sec. III to the results of our close coupling calculations on the HF-HF system. In Sec. IV we attempt to fit the cross sections obtained in our experiments, in which the rotational levels of the hydrogen halide target are neither selected nor resolved. In Sec. V we carry out a comparable fit to the reduced set of theoretical cross sections which results from an equivalent thermal average of the individual $j_a j_b \rightarrow j'_a j'_b$ ACS cross sections for the HCl-HCl system. We then take this fit to the partially averaged theoretical cross sections and attempt to reproduce the underlying fully resolved values. A short conclusion follows.

II. ENERGY GAP MODELS

For the degeneracy-averaged cross section appropriate to the rotationally inelastic collision of two diatomic molecules both the exponential gap (EG) and the power law (PL) models can be summarized in the following equation:

$$\sigma_{j_a j_b \rightarrow j'_a j'_b}(\mathcal{E}) = N \sigma_{j_a j_b \rightarrow j'_a j'_b}^0(E') f(\Delta E/\mathcal{E}), \quad (1)$$

where \mathcal{E} denotes the total energy, E' denotes the final translational energy, and ΔE , the energy gap, represents the absolute value of the difference between the initial and final internal (rotational) energies of the bimolecular system. The quantity N is an overall normalization constant which is independent of the parameters describing the initial state, since the initial density of states is constant for degeneracy averaged cross sections at a given translational energy.³⁷ In the present applications the units of energy will be eV and the units of length Å, so that the normalization constant N will have dimensions Å eV^{-1/2}. In Eq. (1) the "prior" or statistical cross section σ^0 is proportional to the final density of states and is given by

$$\sigma_{j_a j_b \rightarrow j'_a j'_b}^0 = [j'_a][j'_b](\mathcal{E} - \epsilon')^{1/2}, \quad (2)$$

where $[x] = 2x + 1$, and ϵ' denotes the final internal rotational energy of the bimolecular system.

In the EG model the dependence on the energy gap is given by^{6,8}

$$f^{\text{EG}}(\Delta E/\mathcal{E}) = \exp(-\theta \Delta E/\mathcal{E}), \quad (3)$$

and, in the PL model,²² by

$$f^{\text{PL}}(\Delta E/\mathcal{E}) = (\Delta E/\mathcal{E})^{-\gamma}. \quad (4)$$

A consequence of Eq. (2) is that a plot of the information content or "surprisal," defined as⁶

$$I(\Delta E) = -\ln(\sigma_{j_a j_b \rightarrow j'_a j'_b}/\sigma_{j_a j_b \rightarrow j'_a j'_b}^0), \quad (5)$$

will be linear on a semilog or log-log plot if Eq. (3) or Eq. (4), respectively, is valid. Our definition of the prior is consistent with the "least-biased" assumption that all final m_j states are accessible. Imposition of an m_j or helicity-conserving dynamical constraint, as has been proposed by several authors,^{22,23,25} would result in different rotational degeneracy factors in Eq. (2). We note that the form of f^{EG} given in Eq. (3) corresponds to the notation of Levine and Bernstein.^{6,8} The dimensionless parameter θ is called the surprisal parameter. Polanyi and Woodall¹ originally proposed the equivalent expression

$$f^{\text{EG}}(\Delta E) = \exp(-C \Delta E). \quad (6)$$

It is important to observe that for different rotational transitions which have the same ΔE , any energy gap model will predict that for a given initial translational energy the ratio of cross sections is equal to the ratio of final state rotational degeneracies, namely,^{38,39}

$$\frac{\sigma_{j_a j_b \rightarrow j'_a j'_b}}{\sigma_{j_a' j_b' \rightarrow j'_a' j'_b'}} = \frac{[j'_a][j'_b]}{[j'_a'][j'_b']}. \quad (7)$$

This will hold regardless of the explicit form chosen for $f(\Delta E/\mathcal{E})$ in Eq. (1). Thus, in the case of two distinct transitions with a common energy gap, deviations from Eq. (7) will be a direct indication of a breakdown in the statistical approximation which cannot be corrected by the introduction of any multiplicative factor containing a dependence on the energy gap.

III. CLOSE COUPLING CROSS SECTIONS FOR THE HF-HF SYSTEM

In continuation of our earlier study³³ of the HF-HF system, we have recently completed some more extensive full close-coupling (CC) calculations of cross sections for the $j_a j_b = 00 \rightarrow 11, 02, 22, 13$, $j_a j_b = 11 \rightarrow 02, 22, 13$, and $j_a j_b = 22 \rightarrow 13$ transitions.³⁴ The rotational state basis included the $j_a j_b$ pairs 00, 11, 02, 22, 13, 33, 04, 24. As in our earlier work the potential surface consisted of a spherically symmetric and a dipole-dipole term. For more detail we refer the reader to Refs. 33 and 34. Table I presents the results of using both the EG and PL models to fit the CC cross sections at a total energy of 12 500 cm⁻¹ = 1.55 eV. At this high total energy the translational energies in the $j_a j_b = 00, 11$, and 22 initial states are virtually identical. Of the transitions listed above and in Table I we estimate that the CC cross sections are converged with respect to both integration parameters and channel expansion to within $\pm 10\%$ except perhaps for the 00 \rightarrow 13 transition. Accordingly, the cross section for the latter process was not included in the fit. All fits were done using conventional least-squares techniques in a semilog (EG) or log-log (PL) representation. The resulting values of the parameters N [Eq. (1)], θ [Eq. (3)], and γ [Eq. (4)] are listed in Table II.

TABLE I. Fits to close-coupling HF-HF cross sections, $\delta = 12\,500\text{ cm}^{-1}$.

Transition $j_a j_b \rightarrow j'_a j'_b$	Cross section (\AA^2)					
	Statistical prior ^b	Tensorial prior ^c				
	CC ^a	EG ^e	PL ^f	EG ^e	PL ^f	ACS ^d
00 \rightarrow 11	57.6	29.0	22.6	78.7	64.1	45.7
02	9.3	9.8	7.4	47.5	34.8	3.5
22	16.5	11.0	15.1	4.6	12.2	8.4
13 ^g	8.9	5.6	10.4	6.3	9.6	2.1
11 \rightarrow 02	47.7	26.4	30.7	28.9	40.4	28.7
22	13.7	29.7	25.5	12.7	10.0	24.6
13	13.5	15.2	16.0	10.3	9.6	8.7
22 \rightarrow 13	58.7	110.1	128.2	31.0	43.4	32.6
Δ^h		24.6	30.5	21.2	12.2	14.4

^aClose-coupling values from Ref. 34.^bEquation (2).^cEquation (12).^dAdiabatically corrected sudden cross sections; see Ref. 32.^eExponential gap, Eq. (3).^fPower law, Eq. (4).^gThe cross section for this transition is possibly not converged; consequently this cross section was not used in the EG and PL fits.^hRoot-mean-square error in \AA^2 ; $\Delta = [\sum_{i=1}^N (\sigma_i - \bar{\sigma})^2 / (N-1)]^{1/2}$ with N equal to the number of cross sections ($N=8$).

The large values of the parameter θ indicate that the final rotational state distributions are highly nonstatistical. Even in this high energy sudden limit the cross sections deviate significantly from the expected⁷ prior values. It is clear that neither the exponential gap nor power law models provide a truly satisfactory representation of the theoretical cross sections. In particular, the agreement is poorest for the strong dipole-dipole allowed transitions 00 \rightarrow 11, 11 \rightarrow 02, 22 \rightarrow 13. This most likely reflects a serious inaccuracy in the statistical prior [Eq. (2)], specifically in the treatment of the rotational quantum numbers. As we have discussed previously³⁸ as well as in Sec. II [Eq. (7)], since the 11 \rightarrow 02 and 22 \rightarrow 13 transitions have the same energy defect, $2B_0$, any energy gap model incorporating only the final state rotational degeneracy factors, $(2j'_a + 1) \times (2j'_b + 1)$, will predict a cross section ratio

$$\sigma_{22 \rightarrow 13} / \sigma_{11 \rightarrow 02} = 4.2, \quad (8)$$

whereas the true ratio is 1.2. We point out that the latter small value is not a coincidental artifact of the particular collision energy chosen, but remains virtually constant over the entire energy range covered in our CC calculations ($\delta = 3900\text{--}12\,500\text{ cm}^{-1}$).³⁴ Since the 11 \rightarrow 02 and 22 \rightarrow 13 energy gaps are identical, the deviation from the statistical prior uncovered here cannot be corrected by a multiplicative factor dependent on the inelastic energy gap.

In fact, there is now reason to believe that the influence of the angular momentum quantum numbers on the magnitude of degeneracy-averaged cross sections can be better understood on the basis of group-theoretic considerations.³⁸⁻⁴² As we have shown,³⁸ it is probably

reasonable to factor the cross section for a bimolecular $j_a j_b \rightarrow j'_a j'_b$ transition as

$$\sigma_{j_a j_b \rightarrow j'_a j'_b}(\mathcal{E}) = \frac{\pi}{k_{j_a j_b}^2} \sum_{K_1 K_2} [j'_a][j'_b] \times \begin{pmatrix} j'_a & K_1 & j_a \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j'_b & K_2 & j_b \\ 0 & 0 & 0 \end{pmatrix}^2 P^{K_1 K_2}(E, E'), \quad (9)$$

where $k_{j_a j_b}$ is the wave vector in the initial channel, $(\begin{smallmatrix} j & K & j \\ 0 & 0 & 0 \end{smallmatrix})$ is a $3j$ symbol, and $P^{K_1 K_2}(E, E')$ is a tensor opacity.³⁸ In certain cases it may also be reasonable to neglect all but the lowest tensor orders, so that Eq. (9) would reduce to³⁸

$$\sigma_{j_a j_b \rightarrow j'_a j'_b}(\mathcal{E}) \approx \frac{\pi}{k_{j_a j_b}^2} [j'_a][j'_b] \times \begin{pmatrix} j'_a & \bar{K}_1 & j_a \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j'_b & \bar{K}_2 & j_b \\ 0 & 0 & 0 \end{pmatrix}^2 P^{\bar{K}_1 \bar{K}_2}(E, E'), \quad (10)$$

TABLE II. Parameters for exponential gap and power law fits.

System	Total energy (eV)	j_a^a	Exponential gap		Power law	
			N^b	θ^c	N^b	γ^d
Close coupling calculations ^e						
HF-HF	1.55		7.00	151	3.07×10^{-3}	1.292
HF-HF ^f	1.55		174	153	2.68×10^{-2}	1.506
Classical trajectory calculation ^g						
HCl-HCl	0.65	2		15.8		
Molecular beam, thermal average ^h						
LiH-HCl	0.74	1	49.6	90.7	1.76×10^{-2}	1.41
LiH-DCI	0.74	1	64.3	84.8	3.51×10^{-2}	1.33
LiH-HCN	0.70	1	184	82.7	3.79×10^{-2}	1.44
ACS, thermal average ⁱ						
LiH-HCl	0.78	1	38.4	99.7	5.37×10^{-3}	1.58
Fluorescence depletion, thermal average ^j						
HCl-HCl	1.30	8		63.0		
Classical trajectory, thermal average						
HCl-HCl ^k	1.30	8		62.9		
HCl-HCl ^k	1.30	0		20.7		
HCl-HCl ^l	1.30	4, 8		45.2		

^aInitial rotational level of resolved molecule under thermally averaged conditions; see Sec. IV and Eq. (14).^bEquation (1); units are $\text{\AA}^2 \text{eV}^{-1/2}$.^cEquation (3).^dEquation (4).^eReference 34.^fFit using tensorial prior, Eq. (12).^gResults from column 2, Table IV of Ref. 5; $j_a=2$, $j_b=8$; the final state of the second molecule (j'_b) is not resolved.^hExperimental thermally averaged [Eq. (14)] cross sections (Table IV) from Ref. 30 (HCl, DCI) and Ref. 31 (HCN).ⁱACS partially averaged cross sections (Table IV).^jExperimental results from Ref. 2; see Table II of Ref. 5.^kThermally averaged results from Table I of Ref. 5.^lThermally averaged results from Ref. 35.

where the superscript tildes denote the minimum allowed values of K_1 and K_2 , namely,

$$\tilde{K}_1 = |j_a - j'_a| \quad (11a)$$

and

$$\tilde{K}_2 = |j_b - j'_b| \quad (11b)$$

The form of Eq. (10) suggests that one might use a "tensorial" rather than "statistical" prior, which would imply replacing Eq. (2) with

$$\sigma_{j_a j_b \rightarrow j'_a j'_b}^0 = [j'_a][j'_b] \begin{pmatrix} j'_a & \tilde{K}_1 & j_a \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j'_b & \tilde{K}_2 & j_b \\ 0 & 0 & 0 \end{pmatrix}^2 (\mathcal{E} - \epsilon')^{1/2}, \quad (12)$$

with \tilde{K}_1 and \tilde{K}_2 given by Eq. (11). An immediate consequence is that the predicted ratio of the 22→13 and 11→02 cross sections is 1.1, in far better agreement with the exact value.

Guided by these considerations, we carried out a new fit to the CC HF-HF cross sections using the tensorial prior to Eq. (12). The results are shown also in Table I and the parameters of the fits are given in Table II. For both the PL and EG models the agreement is considerably better for the first-order dipole-allowed transitions but deteriorates for some of the other transitions, in particular, 00→02, and 00→22, which are both dipole allowed in second order. The relative magnitude of the cross sections for these two transitions is given correctly only when the statistical prior is used.

Our feeling is that a simple one-parameter dependence on the energy gap is insufficiently flexible to describe adequately the details of the initial and final rotational state dependence of cross sections for polar molecule collisions, where the magnitude of the individual cross sections is governed by several competing factors such as the degree of energy resonance, the order of the dipole-dipole coupling, and the initial and final rotational quantum numbers. The considerable scatter seen in Table I is reminiscent of the recent article by Green,²⁶ where a linear surprisal analysis was made of close-coupling cross sections for rotationally inelastic He-H₂O and He-H₂CO collisions. From the poor quality of the exponential gap fits, Green concluded²⁶ that in the case of these nonlinear molecules the inelastic energy gap was no longer an appropriate independent variable for the representation of the cross sections, possibly a consequence of the extra rotational degree of freedom.

It is also of interest to note that the values of the surprisal parameter θ for our HF-HF calculations are nearly 10 times larger than the value reported by Polanyi and Sathyamurthy⁵ in their classical trajectory study of the similar HCl-HCl system. This comparison is made in Table II. Although this difference could be attributed to many factors (differences in the potential surface, collision energy, or treatment of the dynamics), the size of the discrepancy suggests that it may be unreasonable to use a set of EG or PL parameters to extrapolate from one system to another.

Energy gap models will be of most use only if it is

possible to predict accurately the relevant parameters without recourse to experiment or sophisticated calculations. Although Levine and collaborators have proposed several such methods,^{7,11} it is not yet clear whether at the present state of development they could be used to reproduce the fits shown in Table I without prior knowledge of the CC results. Thus, in terms of predictive power, energy gap models may still be of less practical utility than any dynamical approximation technique which can directly provide reasonably accurate cross sections. To illustrate this point we also compare in Table I the CC cross sections with the predictions of the adiabatically corrected sudden (ACS) method which we have recently developed.³² The details and the application to HF-HF collisions have been given elsewhere.³² It is clear from Table I that the ACS cross predictions provide as good or better a fit to the CC values than the various energy gap models. Obviously, then, the ACS method is to be preferred because of its predictive ability. It should be further noted that the ACS calculations are roughly a factor of 500–1000 faster than the CC calculations.

Although the energy gap models may not yet be capable of absolute predictions, it may be argued that they could be used to extrapolate over a range of collision energies. This would allow one to obtain an accurate description of the energy dependence of $R-T, R$ cross sections without the expense of a closely spaced grid of close coupling calculations. To investigate this possibility we used the EG and PL fits to our HF-HF CC cross sections at $\mathcal{E} = 12\,500\text{ cm}^{-1} = 1.55\text{ eV}$ (Tables I and II) to predict the same cross sections at $\mathcal{E} = 9500\text{ cm}^{-1} = 1.18\text{ eV}$. In keeping with the work of Procaccia and Levine,⁷ we have assumed that in the high energy limit the normalization constant in the EG model [(Eq. (1))] is independent of energy and that the surprisal parameter θ varies linearly with \mathcal{E} , so that

$$\theta(\mathcal{E} = 9500\text{ cm}^{-1}) = 0.76\theta(\mathcal{E} = 12\,500\text{ cm}^{-1}). \quad (13)$$

In the absence of any discussion in the literature, we assumed that the PL parameter γ was independent of energy. Table III presents the comparison with the corresponding CC values and with the ACS predictions. The overall agreement of the PL predictions is somewhat poorer than in the case of the original fit at $\mathcal{E} = 12\,500\text{ cm}^{-1}$, in particular for the directly dipole-coupled transitions. For the EG model the agreement is comparable to that at $\mathcal{E} = 12\,500\text{ cm}^{-1}$, which gives support to the linear scaling of the surprisal parameter [Eq. (13)]. We note that the ACS predictions are now more accurate than those of all the energy gap models, which illustrates again the advantage of a computationally rapid approximation technique with predictive power.

IV. EXPERIMENTAL LiH-DCI, HCl, HCN CROSS SECTIONS

During the past year we have published the results^{30,31} of a series of experimental studies involving collisions of rotationally state-selected, supersonic beams of LiH ($j=1$) with the polar targets HCl, DCI, and HCN. Since the rotational state of the target is neither initially selected nor subsequently resolved, these experiments

TABLE III. Predicted^a HF-HF cross sections, $\delta = 9500 \text{ cm}^{-1}$.

Transition $j_a j_b \rightarrow j'_a j'_b$	Cross section (\AA^2)					ACS ^e
	CC ^b	EG ^c	PL ^e	EG ^f	PL ^g	
00 \rightarrow 11	61.0	25.2	13.8	68.9	37.7	45.5
02	10.0	8.5	4.6	41.6	20.4	3.7
22	12.4	9.5	9.2	9.2	7.1	8.4
13	5.1	4.8	6.3	5.5	5.6	2.1
11 \rightarrow 02	53.1	22.9	18.7	25.2	23.8	30.5
22	12.7	25.6	15.5	11.1	5.8	23.3
13	10.5	13.0	9.8	9.1	5.6	9.0
22 \rightarrow 13	64.4	95.5	78.0	27.0	25.5	34.8
Δ^h		21.9	22.8	21.6	21.1	16.1

^aExponential gap and power law predictions based on fits to the same set of CC cross sections at $\delta = 12500 \text{ cm}^{-1}$ (Tables I and II). The normalization constants [Eq. (1)] and power law parameter γ [Eq. (4)] are unchanged from the values corresponding to the fit at $\delta = 12500 \text{ cm}^{-1}$. The surprisal parameter θ [Eq. (3)] was adjusted according to Eq. (13).

^bClose-coupling values from Ref. 34.

^cEquation (2).

^dEquation (12).

^eAdiabatically corrected sudden sections; Ref. 32.

^fExponential gap, Eq. (3).

^gPower law, Eq. (4).

^hRoot-mean-square error in \AA^2 ; see Footnote h to Table I.

measure only the thermally averaged cross sections, defined by³⁰

$$\sigma_{j_a \rightarrow j'_a} = Z_b(T)^{-1} \sum_{j_b j'_b} (2j_b + 1) \sigma_{j_a j_b \rightarrow j'_a j'_b} \exp(-\epsilon_{j_b}/kT), \quad (14)$$

where Z_b is the rotational partition function of the target gas at temperature T . Other experiments^{2,19,20} measure similar partially averaged cross sections or rate constants, and have been interpreted in terms of the inelastic energy gaps of the resolved molecule. Accordingly, we have attempted to fit our experimental $j_a \rightarrow j'_a$ cross sections [Eq. (14)] to the functional form

$$\sigma_{j_a \rightarrow j'_a} = A(2j'_a + 1)f(\Delta E_a), \quad (15)$$

where ΔE_a is the energy gap of the LiH molecule. Both power law and exponential dependences on ΔE_a were used. In Eq. (15) the suppression of the rotational degeneracy of the unresolved molecule is consistent with published analyses^{20,21} of experiments which measure these partially averaged cross sections.⁴³

The results of this fit are displayed in Table IV and the corresponding parameters are given in Table II. The dependence on the energy gap is clearly better represented by a power than by an exponential. In fact, the power law fit lies within the experimental error bars. However, the lack of an algorithm for predicting the power law parameters remains a serious drawback. Also, one wonders whether there is a reasonable physical explanation for the significant differences in the values of the power γ [Eq. (4)] corresponding to the HCl and DCl cross sections, or whether this is purely an artifact of the fitting process.

Table IV also compares the experimental cross sections with values obtained by using the ACS approximation to determine the individual $j_a j_b \rightarrow j'_a j'_b$ cross sections in Eq. (14). We note that the agreement is as good if not better than that found for the EG model, although not as good as that for the PL model. However, as we have discussed at the end of Sec. III, the *predictive* capability of the ACS method is a significant advantage and in our opinion outweighs the reduced accuracy of the smaller cross sections corresponding to large Δj .

It is also worthwhile to compare with our results the

TABLE IV. Rotationally inelastic, thermally averaged LiH ($j_a = 1 \rightarrow j'_a$) + HCl, DCl, HCN ($T = 298 \text{ K}$) cross sections.

Transition $j_a = 1 \rightarrow j'_a$	Cross section (\AA^2) ^a			
	Experiment ^b	EG fit ^c	PL fit ^d	ACS ^e
1 \rightarrow 0	64 \pm 9	35	77	58
2	157 \pm 23	143	144	121
3	67 \pm 12	105	56	43
4	33 \pm 7	57	31	18
5	23 \pm 4	24	20	11
6	11 \pm 5	7.8	14	6.7
χ^2/ν^f		8.2	1.1	3.5
Δ^g		24.7	9.8	21.6
DCl				
1 \rightarrow 0	88 \pm 11	47	99	73
2	203 \pm 32	190	196	152
3	93 \pm 16	146	81	48
4	53 \pm 13	84	47	22
5	29 \pm 6	37	32	18
6	21 \pm 3	13	23	8.4
χ^2/ν^f		9.9	0.6	6.5
Δ^g		33.8	8.6	35.0
HCN				
1 \rightarrow 0	245 \pm 30	124	277	208
2	519 \pm 88	496	509	419
3	222 \pm 47	363	191	116
4	125 \pm 26	196	105	57
5	64 \pm 17	81	68	33
6	41 \pm 12	26	48	22
χ^2/ν^f		8.9	0.6	3.4
Δ^g		90.6	22.5	75.9

^aEquation (14).

^bExperimental values from Ref. 30 (HCl, DCl) and Ref. 31 (HCN); the total energies are 0.74 eV (HCl, DCl) and 0.70 eV (HCN).

^cEquation (15) using $f(\Delta E_a) = \exp(-\theta \Delta E_a/\delta)$.

^dEquation (15) using $f(\Delta E_a) = (\Delta E_a/\delta)^{-\gamma}$.

^eCross sections calculated using adiabatically corrected sudden method to determine the individual $j_a j_b \rightarrow j'_a j'_b$ cross sections in Eq. (14); values taken from Table II of Ref. 30 (HCl, DCl) and Table III of Ref. 31 (HCN).

^fChi-squared defined as in Eq. (32) of Ref. 23. The parameter ν is defined as the number of data points minus the number of free parameters and is thus equal to 4 for the EG and PL fits and equal to 6 for the ACS values.

^gRoot-mean-square error in \AA^2 ; defined as in Footnote h of Table I with $N = 6$.

TABLE V. Rotationally inelastic LiH ($j_a=1$) + HCl ($j_b=2$) cross sections.

j'_a	j'_b	Cross section (\AA^2)		
		ACS ^a	PL fit ^b	EG fit ^c
0	1	25.3	24.1	41.7
	3	42.2	72.7	110.9
	5	1.8	9.1	8.7
2	1	95.8	1361	420.4
	3	54.4	128.5	273.2
	5	5.4	34.5	21.5
	7	1.1	15.8	0.4
3	0	8.1	39.2	198.1
	2	22.3	71.7	365.1
	4	11.3	39.7	64.0
	6	2.6	21.8	2.4
	8	0.7	13.0	0.0
4	1	7.4	100.4	213.2
	3	6.1	69.9	94.3
	5	4.4	37.5	7.4
	7	1.5	21.5	0.1

^aAdiabatically corrected sudden values (Ref. 32).

^bValues predicted from power law fit to thermally averaged ACS values (Table IV); fit parameters given in Table II.

^cValues predicted from exponential gap fit to thermally averaged ACS values (Table IV); fit parameters given in Table II.

values of the surprisal parameters θ obtained in earlier experimental² and classical trajectory^{5,35} determinations of thermally averaged rotationally inelastic cross sections in the HCl-HCl system. This comparison appears in Table II. One is struck by the large variation in the values of θ , particularly among the various classical trajectory determinations. This variation most likely reflects differences in the potential surfaces used, and indicates, at least for polar collision systems, that θ can not be assumed to be independent of the nature of the collision partner. It is worthwhile observing that this assumption underlies the method proposed by Procaccia and Levine⁷ for the synthesis of the surprisal parameter without any dynamical input. The results displayed in Table II suggest that this method will probably not be reliable for polar systems at hyperthermal velocities.

V. DECONVOLUTION OF THERMALLY AVERAGED EXPERIMENTS

Although it is not yet possible to deduce accurate EG or PL parameters directly from the Hamiltonian,⁴⁴ nevertheless one might argue that these models could be used to predict reasonably accurate, fully state resolved cross sections from a fit to partially averaged quantities such as those given by Eq. (14). If this were true, then the EG or PL models could ultimately provide valuable insight into the fundamental cross sections which themselves are not experimentally accessible. To investigate this possibility we carried out PL and EG fits to the partially thermally averaged ACS $j_a \rightarrow j'_a$ cross sections [Eq. (14)] for the LiH-HCl system (Table IV). The re-

sulting parameters are given in Table II. We then used these values of N , θ , and γ with the statistical prior of Eq. (2) and with the full $j_a j_b \rightarrow j'_a j'_b$ energy gap to predict the fully resolved $j_a j_b \rightarrow j'_a j'_b$ cross sections. A comparison with a representative sample of the original ACS values appears in Table V.

It is obvious that the thermal fits considerably overestimate the fully resolved cross sections. Since the differences are much larger than the expected errors in the ACS cross section themselves, which can be crudely estimated from inspection of Table I, it is highly unlikely that either the PL or EG fits to the *experimental* partially averaged cross sections (Table IV) would provide accurate estimates of the true state-resolved cross sections. Also, we see in Table V that the fits to the averaged cross sections furnish at best only a poor representation of the j'_b dependence of the fully resolved cross sections.

An important corollary is that there may be little justification in using either EG or PL fits to thermally averaged cross sections, such as those defined by Eq. (14), to interpret or simulate experiments characterized by nonequilibrium rotational distributions of the b molecules. Serious errors could arise because the relevant cross sections would correspond to nonthermal averages of the individual $j_a j_b \rightarrow j'_a j'_b$ cross sections, which are themselves not given accurately by the EG or PL fits to the original thermally averaged quantities.

VI. CONCLUSIONS

We have applied both the exponential gap and power law models to rotationally inelastic collisions between polar molecules. Neither of these parameterizations was able to fit with high accuracy our recent fully quantum state-resolved cross sections for the HF-HF system. This comparison further revealed a fundamental inaccuracy in the statistical factors used in both these models which cannot be corrected by the introduction of a multiplicative factor dependent solely on the energy gap. Unfortunately, even when the angular momentum quantum numbers are treated within a tensorial framework based on group theory, the accuracy of the fits is not greatly improved. This indicates that the fine details of the dynamics of rotational energy transfer between polar molecules can not be satisfactorily reduced to a simple dependence on the inelastic energy gap. Additionally, the present lack of available prescriptions for the accurate prediction of EG or PL parameters directly from the interaction potential represents a severe limitation, especially in view of the existence of simple dynamical approximation techniques, such as the adiabatically corrected sudden approximation,³² which can be used to generate directly, without excessive computational effort, cross sections which are as accurate as the EG or PL fits.

In our recent experiments^{30,31} involving lithium hydride the rotational state of the collision partner is neither selected nor resolved. The appropriate partially averaged cross sections can be fit extremely well by a power law dependence on the energy gap of the resolved molecule. Again, however, a major drawback is the in-

ability to predict, prior to doing the experiment, the power law parameters or their variation with collision partner. Thus it is difficult to decide whether there is an underlying physical basis for the good agreement of the power law model. Furthermore, using our previously computed³² ACS cross sections, we were able to show that neither the PL nor EG fits to partially averaged cross sections can be used to predict, with any degree of accuracy, the more fundamental fully resolved cross sections.

In our opinion, attention should be given to the development of more accurate techniques for the *ab initio* derivation of the PL or EG parameters, or, at the least, to the development of methods for predicting the variation of these parameters from system to system. It is worthwhile to point out that an alternative approach toward the interpolation and extrapolation of $R \rightarrow T, R$ cross section matrices is given by the scaling relations developed by DePristo and co-workers.^{39,40} These are based on a physically reasonable extension of the sudden scaling relations³⁹⁻⁴² discussed in Sec. III and do not assume a simple explicit dependence on the inelastic energy gap. A preliminary application to the HF-HF system has been made.⁴⁰

ACKNOWLEDGMENTS

The research described here was supported by the National Science Foundation, Grant CHE-7808729; by the U.S. Army Research Office, grant DAAG29-78-G-1110; by the Computer Science Center and General Research Board, University of Maryland; and by the National Resource for Computation in Chemistry under a grant from the National Science Foundation and the Basic Energy Sciences Division of the United States Department of Energy under Contract No. W-7405-ENG-48.

- ¹J. C. Polanyi and K. B. Woodall, *J. Chem. Phys.* **56**, 1563 (1972).
- ²A. M. G. Ding and J. C. Polanyi, *Chem. Phys.* **10**, 39 (1975).
- ³N. C. Lang, J. C. Polanyi, and J. Wanner, *Chem. Phys.* **24**, 219 (1977); B. A. Esche, R. E. Kutina, N. C. Lang, J. C. Polanyi, and A. M. Rulis, *ibid.* **41**, 183 (1979).
- ⁴J. C. Polanyi, N. Sathyamurthy, and J. L. Schreiber, *Chem. Phys.* **24**, 105 (1977); J. C. Polanyi and N. Sathyamurthy, *ibid.* **29**, 9 (1978).
- ⁵J. C. Polanyi and N. Sathyamurthy, *J. Phys. Chem.* **83**, 978 (1979).
- ⁶R. D. Levine, *Ann. Rev. Phys. Chem.* **29**, 59 (1978), and references therein.
- ⁷I. Procaccia and R. D. Levine, *J. Chem. Phys.* **64**, 808 (1976).
- ⁸I. Procaccia and R. D. Levine, *Physica (Utrecht) A* **82**, 623 (1975); R. D. Levine, R. B. Bernstein, P. Kahana, I. Procaccia, and E. T. Upchurch, *J. Chem. Phys.* **64**, 796 (1976).
- ⁹M. D. Pattengill and R. B. Bernstein, *J. Chem. Phys.* **65**, 4007 (1976).
- ¹⁰D. F. Heller, *Chem. Phys. Lett.* **45**, 64 (1977).
- ¹¹Y. Alhassid and R. D. Levine, *Phys. Rev. A* **18**, 89 (1978).
- ¹²B. C. Sanctuary, *Chem. Phys. Lett.* **62**, 378 (1978).
- ¹³I. Procaccia, Y. Shimon, and R. D. Levine, *J. Chem. Phys.* **63**, 3181 (1975).
- ¹⁴R. J. Hall, *IEEE J. Quantum Electron.* **QE-12**, 453 (1976).
- ¹⁵L. H. Sentman, *J. Chem. Phys.* **67**, 966 (1977).
- ¹⁶K. Koura, *J. Chem. Phys.* **67**, 1275 (1977).
- ¹⁷A. Ben-Shaul, S. Feliks, and O. Kafri, *Chem. Phys.* **36**, 291 (1979).
- ¹⁸W. H. Duerwer and D. W. Setser, *J. Chem. Phys.* **58**, 2310 (1973).
- ¹⁹J. J. Hinchin and R. H. Hobbs, *J. Chem. Phys.* **65**, 2732 (1976); J. J. Hinchin, *J. Appl. Phys.* **50**, 628 (1979).
- ²⁰J. C. Gautier, J. P. Geindre, J. P. Moy, and J. F. Delpech, *Phys. Rev. A* **13**, 1781 (1976); J. F. Delpech, J. C. Gautier, and F. Devos, *J. Chem. Phys.* **67**, 5934 (1977).
- ²¹B. E. Wilcomb and P. J. Dagdigan, *J. Chem. Phys.* **67**, 3829 (1977).
- ²²T. A. Brunner, R. D. Driver, N. Smith, and D. E. Pritchard, *Phys. Rev. Lett.* **41**, 856 (1978); M. Wainger, I. Al-Agil, T. A. Brunner, A. W. Karp, N. Smith, and D. E. Pritchard, *J. Chem. Phys.* **71**, 1977 (1979).
- ²³T. A. Brunner, R. D. Driver, N. Smith, and D. E. Pritchard, *J. Chem. Phys.* **70**, 4155 (1979).
- ²⁴D. E. Pritchard, N. Smith, R. D. Driver, and T. A. Brunner, *J. Chem. Phys.* **70**, 2115 (1979).
- ²⁵R. Goldflam and D. J. Kouri, *J. Chem. Phys.* **65**, 4218 (1976).
- ²⁶S. Green, *Chem. Phys.* **40**, 1 (1979).
- ²⁷E. F. Jendrek and M. H. Alexander, *J. Chem. Phys.* **72**, 6452 (1980).
- ²⁸A. Kafri and R. Kosloff, *Chem. Phys.* **23**, 257 (1977).
- ²⁹Attempts to obtain the exponential gap parameters directly from the Hamiltonian have been explored by Alhassid and Levine (Ref. 11).
- ³⁰P. J. Dagdigan, B. E. Wilcomb, and M. H. Alexander, *J. Chem. Phys.* **71**, 1670 (1979).
- ³¹P. J. Dagdigan and M. H. Alexander, *J. Chem. Phys.* **72**, 6513 (1980).
- ³²M. H. Alexander and A. E. DePristo, *J. Phys. Chem.* **83**, 1499 (1979); M. H. Alexander, *J. Chem. Phys.* **71**, 1683 (1979).
- ³³A. E. DePristo and M. H. Alexander, *J. Chem. Phys.* **66**, 1334 (1977).
- ³⁴M. H. Alexander, *J. Chem. Phys.* (to be published).
- ³⁵A. F. Turfa and R. A. Marcus, *J. Chem. Phys.* **70**, 3035 (1979).
- ³⁶See, for example, R. J. Cross, Jr., *J. Chem. Phys.* **59**, 510 (1971).
- ³⁷For a further discussion of the independence of the normalization constant N from the initial rotational quantum numbers, see A. E. DePristo and H. Rabitz, *J. Chem. Phys.* **69**, 902 (1978).
- ³⁸M. H. Alexander, *J. Chem. Phys.* **71**, 5212 (1979).
- ³⁹A. E. DePristo, S. D. Augustin, R. Ramaswamy, and H. Rabitz, *J. Chem. Phys.* **71**, 850 (1979).
- ⁴⁰A. E. DePristo and H. Rabitz, *J. Chem. Phys.* **72**, 4685 (1980).
- ⁴¹R. Goldflam, S. Green, and D. J. Kouri, *J. Chem. Phys.* **67**, 4149 (1977); R. Goldflam, D. J. Kouri, and S. Green, *ibid.* **67**, 5661 (1977); R. Goldflam and D. J. Kouri, *ibid.* **70**, 5076 (1979).
- ⁴²J. M. Launay, *Chem. Phys. Lett.* **72**, 152 (1980).
- ⁴³Recently, C. Gayatri and N. Sathyamurthy [*Chem. Phys.* **48**, 227 (1980)] have discussed the choice of statistical prior in the case where both states of molecule a but only the initial state of molecule b are resolved.
- ⁴⁴For dipole-dipole collisions Alhassid and Levine (Ref. 11) have shown how within a time dependent sudden (TDS) treatment of the dynamics it is possible to deduce θ directly from the Hamiltonian. Unfortunately, the TDS approximation is known to be inaccurate for hyperthermal rotationally inelastic collisions between polar molecules (Refs. 30-32).