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N₂-H₂ isotropic Raman Q-branch linewidths: an Energy-Corrected Sudden scaling law

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The Energy-Corrected Sudden (ECS) model has been widely developed to calculate rovibrational Raman linewidths as well as the overlap between lines through the off-diagonal elements of the relaxation matrix. The accuracy of the results depends on the precision of the input data on which the ECS parameters are fitted. Starting from recent experimental and theoretical data for nitrogen (N₂) Q-branch perturbed by hydrogen from 77 to 580 K, we have determined the ECS parameters for this molecular system and calculated systematically the N₂-H₂ line broadening coefficients for $J = 0$ to 20 up to 2000 K, which will be useful for combustion diagnostics purposes.

KEYWORDS: stimulated Raman spectroscopy; collisional line broadening; nitrogen-hydrogen mixture; Energy-Corrected Sudden model

INTRODUCTION

Stimulated Raman scattering from nitrogen is an improved technique for the purpose of temperature and concentration diagnostics in atmospheric and combustion media. For practical applications, precise studies of the collisional processes involving N₂ as an active molecule are needed, from low temperatures for atmospheric purposes up to very high temperatures in combustions. But the diagnostics is complicated by the phenomenon of ‘motional narrowing’ that arises in the nitrogen isotropic Raman Q-branch. The Q-branch band shape has to be analyzed through rotational relaxation models such as the Energy-Corrected Sudden (ECS) model.^{1,2} The pure nitrogen isotropic Raman linewidths have been measured with high accuracy several years ago,^{3,4} as well as those of N₂-CO₂⁵ and N₂-H₂O⁶ mixtures. Concerning flame thermometry, the line broadening values of nitrogen by hydrogen are also required.⁷ Since very few experimental data were available, self-broadened N₂ linewidths instead of N₂-H₂ ones were commonly used in rovibrational thermometry.⁸

The present work, devoted to N₂-H₂, is based on a previous extensive experimental and theoretical study for the collisional line broadening coefficients of this molecular system.^{9,10} The experimental measurements were obtained from high-resolution stimulated Raman spectra recorded

in Madrid at the temperatures of 77, 298, 440, and 580 K. The corresponding theoretical calculations, using an *ab initio* calculation of the potential energy surface (PES),¹¹ have been done with the exact close-coupling (CC) method for the three lower temperatures as the computational time remains reasonable until 440 K, and with a coupled-states (CS) treatment at 580 K. The overall agreement^{10,12} obtained between experimental and theoretical linewidth values then allows us to build ECS models using three different scaling laws. Finally, the model that gives the best agreement with the input data is used to calculate with reasonable confidence the $Q(J)$ linewidths up to $J = 20$ and $T = 2000$ K, which will be essential for combustion purpose.

THE ECS MODEL

The dynamical scaling law, originally proposed by Goldflam *et al.*¹³ to describe the rotational excitation of a simple system, is based on the so-called Infinite Order Sudden (IOS) approximation. The molecule is assumed not to rotate during the collision, which results in an important simplification of the quantum mechanical equations for molecular scattering. Let us consider here the case of isotropic Raman scattering. For a diatomic molecule, it leads to the following relation between the off-diagonal matrix elements $W_{j_i j'_i}^{(IOS)}(T)$ and the basis rate constants $Q_\lambda(T)$:

$$W_{j_i j'_i}^{(IOS)}(T) = [2j'_i + 1] \sum_{\lambda} [2\lambda + 1] \begin{pmatrix} j_i & j'_i & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 Q_\lambda(T) \quad (1)$$

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where λ is one component of the intermolecular potential developed on Legendre polynomial basis and $\left\{ \begin{matrix} - & - & - \\ - & - & - \end{matrix} \right\}$ is a 3-j symbol. In particular, for $j'_i = 0$, we have $W_{j_0}^{(IOS)}(T) = Q_\lambda(T)$, which represents the transition probability from j_i to 0. Equation (1) means that the entire rotational relaxation matrix is determined by the knowledge of a single column. But the applicability of the IOS approximation is restricted to molecular systems for which the duration of the collision is very short compared to the rotational period of the diatom, such as CO–He for instance. For most other systems, the finite duration of the collision has to be introduced. De Pristo *et al.*¹ have therefore proposed an adiabatic correction to the IOS scaling law and the resulting equation is:

$$W_{j_i j'_i}^{(ECS)}(T) = [2j'_i + 1] e^{-\frac{E_{j_{i>}} - E_{j_i}}{kT}} \Omega_{j_{i>}}^2 \times \sum_{\lambda} [2\lambda + 1] \begin{pmatrix} j_i & j'_i & \lambda \\ 0 & 0 & 0 \end{pmatrix} \frac{Q_\lambda(T)}{\Omega_\lambda^2} \quad (2)$$

where $j_{i>}$ is the largest number of j_i and j'_i , and the adiabaticity factor Ω_j is given for a homonuclear molecule by:

$$\Omega_j = \frac{1}{1 + \frac{\omega_{j,j-\delta}^2 \ell_c^2}{24\bar{v}^2}} \quad (3)$$

In Eqn (3), $\omega_{j,j-\delta}$ is the frequency of the transition to the nearest level ($\delta = 2$ for a homonuclear molecule), ℓ_c characterizes the interaction length, \bar{v} is the mean collision velocity of the molecular pair given by the Maxwell–Boltzmann statistics at a given temperature T :

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}} \quad (4)$$

where μ is the reduced mass of the system. The term $\ell_c^2/\bar{v}^2 = \tau_c^2$ represents the square of the effective duration of collisions.

The transfer rates $Q_\lambda(T)$ may be represented by simple analytical forms. The resulting laws are called ECS-EP, ECS-P, or ECS-E following the choice of the empirical form. Starting from the exponential-polynomial law (EP) proposed by Millot² and Bonamy *et al.*¹⁴

$$Q_\lambda(T) = A_0 \left(\frac{T}{T_0} \right)^{-N} \frac{e^{-\frac{\beta E_\lambda}{kT}}}{[\lambda(\lambda + 1)]^\gamma} \quad (5)$$

where T_0 is a reference temperature ($T_0 = 296$ K), one gets the polynomial law (P) by putting $\beta = 0$ and the exponential law (E) for $\gamma = 0$.

Equation (5) shows the four fitting parameters (N , β , γ , A_0). Let us recall that the scaling length ℓ_c is an additional one. These five parameters have to be determined from linewidth data (experimental and/or theoretical).

RESULTS AND DISCUSSION

The N₂–Q branch collisional line broadening coefficients have been measured by stimulated Raman loss spectroscopy in Madrid^{9,15} for a large set of temperatures and rotational quantum numbers, (between 77 and 580 K and for $J = 22$ for the highest temperature). The corresponding linewidth calculations may be performed using two main *ab initio* approaches. At high temperature, the semiclassical approach⁹ is the only tractable one and is commonly used for a large variety of molecular systems. For lower temperatures, exact pure quantum methods such as CC or CS approaches^{10,12} are available. All these *ab initio* models need an adequate description of the molecular interactions such as the PES, which we have recently introduced in pure quantum approaches for the N₂–H₂ mixture.¹¹ In Ref. 10, we have presented the new results obtained using the CC method (for $T = 77, 298, \text{ and } 440$ K) and the CS method (for $T = 580$ K). The measured and calculated line broadening coefficients are reported in Table 1. As stated in Ref. 10, we obtain satisfactory agreement between experiment and theory, which confirms that the new PES allows us to reproduce quite well the experimental data and their temperature dependence.

Temperature diagnostics in combustion engines requires the values of the collisional broadening coefficient at temperatures higher than 580 K. Owing to the greatly increasing computing time needed when using pure quantum methods, no evaluation of collisional linewidths is reasonably possible at high temperatures. Apart from the semiclassical model already mentioned, approximate methods like ECS scaling laws have shown their usefulness. In this work, we propose to use the ECS scaling laws to calculate the rovibrational linewidths for N₂ perturbed by H₂ in a large temperature range. The first step of the calculation consists in the determination of the parameters (N , β , γ , A_0 and ℓ_c) describing the ECS scaling laws (*cf* Eqn (5)). Note that only four parameters must be fitted for ECS-E ($\gamma = 0$) and ECS-P ($\beta = 0$) laws. To evaluate the temperature power law introduced in the transfer rates $Q_\lambda(T)$ (*cf* Eqn (5)), a grid of values for different temperatures is needed. In this study, four temperatures (77, 298, 440, and 580 K) were investigated.^{11,12} Using the calculated line broadening coefficients of Table 1, we have obtained a new set of ECS parameters for the three different laws (ECS-E, ECS-P, and ECS-EP). The fitted parameters are reported in Table 2. The Raman Q-branch line broadening coefficients obtained from the fitted parameters are represented in Figs 1 to 4 for $T = 77, 298, 440, \text{ and } 580$ K for ECS-E, ECS-P, and ECS-EP laws. The pure quantum calculations are also reported for comparison.

For all the temperatures studied, we observe good agreement between the pure quantum calculations and the ECS methods. Except for the lowest J values, we can reproduce quite well the J dependence using these three sets of ECS parameters. The ECS-EP law seems to be the most adapted model to describe the temperature dependence

Table 1. Comparison between experimental and theoretical values^{10,11} of the Q-branch line broadening coefficients of the N₂-H₂ system for several J values and temperatures. Calculations were made using the close-coupling (CC) or coupled-states (CS) method depending on the considered temperature.¹⁰ All values are in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$

J	Exp. 77 K	CC 77 K	Exp. 298 K	CC 298 K	Exp. 440 K	CC 440 K	Exp. 580 K	CS 580 K
0	127.48 (28.5)	121.90	58.2 (12.0)	64.08	45.5 (16.4)	53.49	44.9 (39.3)	47.66
1	82.64 (16.2)	74.17	49.5 (9.8)	45.85	36.0 (11.4)	–	50.3 (17.6)	–
2	82.93 (15.4)	85.2	45.4 (4.3)	46.51	36.4 (9.0)	39.60	47.1 (15.0)	35.91
3	78.11 (19.5)	89.24	50.6 (6.9)	48.29	41.6 (10.9)	–	36.5 (17.2)	–
4	84.75 (10.8)	92.39	46.5 (3.8)	49.45	39.0 (11.3)	41.48	25.5 (10.3)	36.69
5	92.69 (12.1)	91.90	44.6 (5.6)	50.13	38.4 (9.0)	–	32.1 (11.8)	–
6	101.82 (16.1)	92.62	47.8 (4.6)	50.56	37.1 (8.3)	42.31	31.2 (11.2)	37.21
7	–	92.62	51.1 (5.4)	50.85	40.1 (6.5)	–	36.5 (11.4)	–
8	–	92.77	46.4 (3.4)	50.97	42.5 (9.0)	42.58	40.2 (10.3)	37.38
9	–	–	50.5 (4.0)	50.92	38.9 (8.1)	–	37.4 (8.3)	–
10	–	–	48.6 (4.0)	50.79	37.3 (9.6)	42.62	35.9 (11.8)	37.45
11	–	–	41.5 (11.2)	50.47	42.6 (6.2)	–	43.3 (10.5)	–
12	–	–	–	–	43.1 (5.3)	–	38.6 (12.6)	37.44
13	–	–	–	–	40.7 (9.5)	–	34.7 (14.0)	–
14	–	–	–	48.87	38.6 (6.7)	41.54	40.1 (9.0)	37.28
15	–	–	–	–	42.9 (9.3)	–	32.2 (11.1)	–
16	–	–	–	–	33.4 (6.1)	–	39.7 (10.6)	36.98
17	–	–	–	–	32.3 (19.6)	–	30.9 (13.4)	–
18	–	–	–	–	34.2 (6.0)	40.27	26.7 (13.3)	36.48
19	–	–	–	–	–	–	22.6 (17.7)	–
20	–	–	–	–	–	–	26.4 (16.1)	35.83
21	–	–	–	–	–	–	39.9 (9.3)	–
22	–	–	–	–	–	–	20.1 (15.5)	35.01

Table 2. Fitting parameters of ECS-E, ECS-P, and ECS-EP^{1,2,14} for N₂ Q-branch perturbed by H₂ using pure quantum calculations of collisional line broadening coefficients.¹⁰ A_0 is expressed in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$; ℓ_C in Å; N , γ , and β are dimensionless

N ₂ -H ₂	A_0	N	γ	β	ℓ_C
ECS-E	3.03	1.6181	0	1.4738	0.4647
ECS-P	72.26	0.7594	1.202	0	0.9291
ECS-EP	46.595	0.8521	1.028	0.167	0.6511

of line broadening coefficient with confidence. Systematic calculations of the N₂-H₂ Q-branch collisional linewidth perturbed by using the ECS-EP law were then performed, and they are reported in Fig. 5 vs the J rotational quantum number for temperatures up to 2000 K.

CONCLUSIONS

The ECS dynamical model has been widely used for the purpose of temperature diagnostics in combustion media. Accurate measurements of the collisional linewidths of the Q-branch lines of N₂ in H₂ have been performed by stimulated

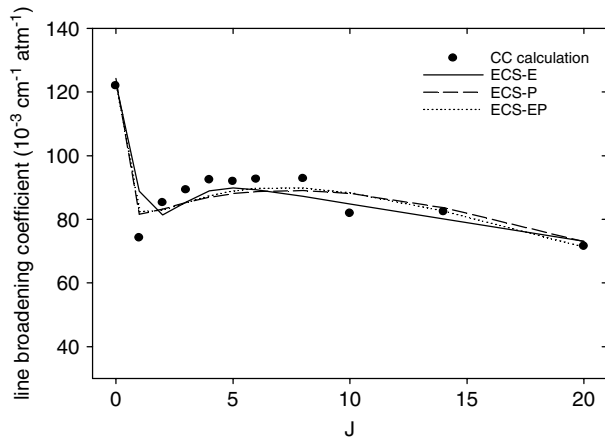


Figure 1. Calculated line broadening coefficient of N₂ Q-branch perturbed by H₂ vs the rotational quantum number J at $T = 77$ K. Comparison between results obtained by pure quantum calculations¹⁰ and those deduced from ECS-E (solid line), ECS-P (dashed line), and ECS-EP (dotted line) laws.^{2,14,15}

Raman loss spectroscopy from 77 to 580 K. A concomitant quantum mechanical CC study using a new, accurate PES has given very good agreement with experiment. Using

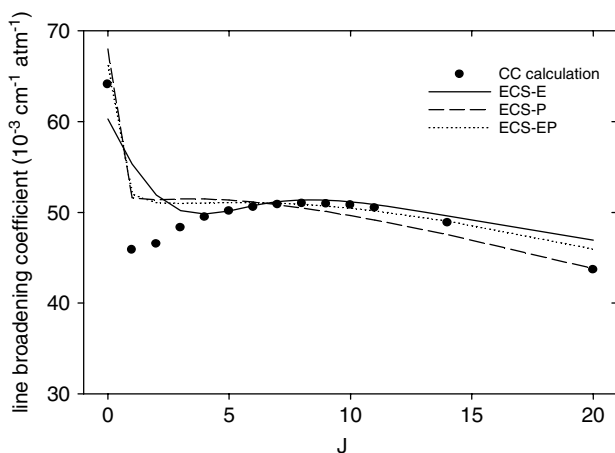


Figure 2. Same as Fig. 1 but at $T = 296$ K.

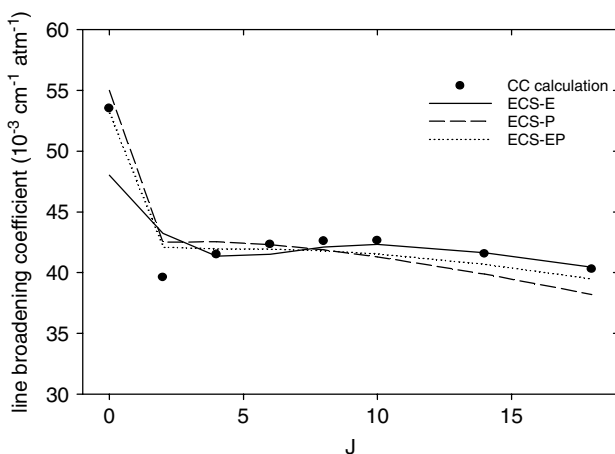


Figure 3. Same as Fig. 1 but at $T = 440$ K.

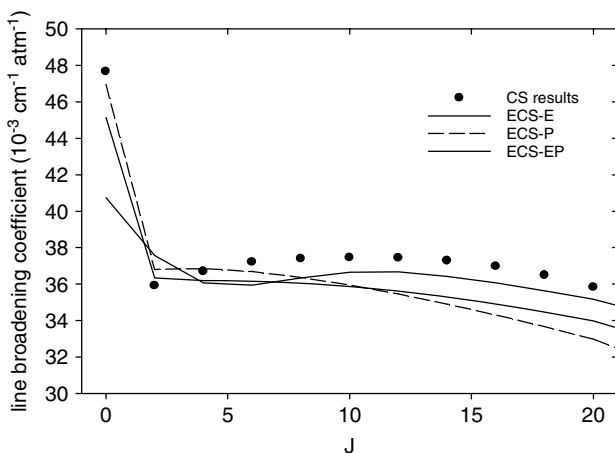


Figure 4. Same as Fig. 1 but at $T = 580$ K.

these data, three different sets of ECS parameters (ECS-E, ECS-P, and ECS-EP) have been obtained, allowing linewidths

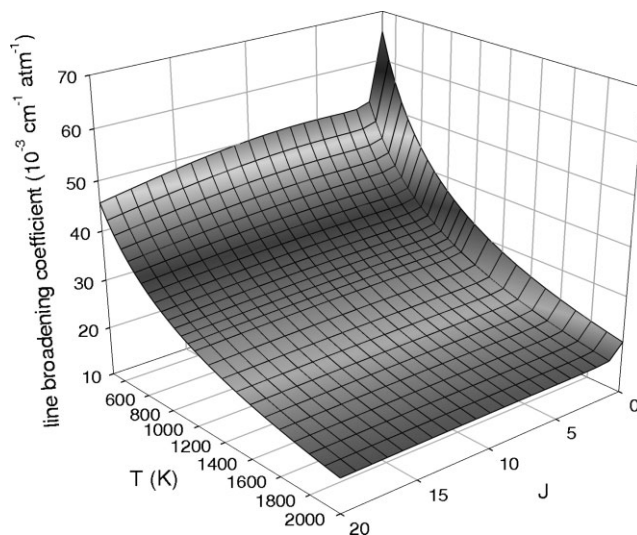


Figure 5. Line broadening coefficient of N_2 Q-branch perturbed by H_2 vs J quantum number and temperature evaluated using the ECS-EP law and the fitting parameters (cf Table 2).

calculations. As the ECS-EP formulation gives the best agreement with the existing data, it has been retained to extrapolate the linewidths values up to 2000 K.

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