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Citation: The Journal of Chemical Physics **109**, 6338 (1998); doi: 10.1063/1.477187 View online: http://dx.doi.org/10.1063/1.477187 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/109/15?ver=pdfcov Published by the AIP Publishing

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Energy corrected sudden calculations of linewidths and line shapes based on coupled states cross sections: The test case of CO_2 -argon

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(Received 10 June 1998; accepted 10 July 1998)

The accuracy of the energy-corrected sudden (ECS) formalism for line shape calculations is investigated, using coupled states calculation for CO2-Ar collisions on the recently developed "single repulsion" potential of Hutson et al. [J. Chem. Phys. 107, 1824 (1997); 105, 9130 (1996)]. Inelastic cross sections $\sigma^0(L \rightarrow 0, E) \equiv Q'_L(E)$ are calculated using the MOLSCAT program, and then averaged over Maxwell-Boltzmann kinetic energy distributions to give the thermally averaged "basic rates" $Q'_{I}(T)$ needed in the ECS formalism. The ECS linewidths for low initial J, J_{i} \leq 16, are sensitive only to the low-L basic rates, for which the CS calculations are converged; comparing them with directly calculated CS linewidths thus gives a stringent test of the ECS model, and it works well (within 10%). However, for higher J_i lines and for band shape calculations, basic rates for higher L are needed for convergence. These are obtained by an extrapolation procedure based on experimental data, using an exponential power law and the adiabaticity factor recently suggested by Bonamy et al. [J. Chem. Phys. 95, 3361 (1991)] ECS calculations using the resulting basic rates are designated "extrapolated CS-ECS calculations," and are found to give accurate results for high-J linewidths, for near-wing absorption and for band profiles over a very wide range of perturber pressures (up to 1000 atm). © 1998 American Institute of Physics. [S0021-9606(98)02138-2]

I. INTRODUCTION

The effects of collisions on molecular line shapes in the gas phase have been the subject of intensive experimental and theoretical studies for 20 years or more.¹ The earlier work concentrated on simple pressure broadening and shifting of spectral lines, but it is now known that line mixing and interference effects are significant for many experiments. These include measurements of infrared and Raman Q branches even at moderate perturber densities, since the lines are closely spaced, and of infrared P and R branches at high densities, where the rotational substructure or even the branch structure itself collapses. The wings of bands are also affected by line mixing even at low densities.

A formal quantum-mechanical theory to describe line broadening and mixing has been available for over 40 years.^{2–5} The effects are governed by a relaxation operator, which provides the connection between the spectral profile and the intermolecular potential energy surface. Within the impact approximation, the frequency-dependent relaxation operator reduces to a frequency-independent relaxation matrix *W* whose elements may be expressed in terms of the *S* matrices of molecular collision theory.⁴ The main factor that limits the accuracy of calculations is that, for most systems, the intermolecular potential is not known accurately. However, once the intermolecular potential is known, the *S* matrices may in principle be calculated using either the "exact" close coupling method⁶ or a variety of quantum approximations^{7,8} such as the coupled-states (CS) and infinite-order sudden (IOS) approximations.

The full calculation has been carried through for a few prototype systems such as CO-He.9 However, for heavier systems, accurate potential surfaces are generally not available, and the CPU times required for close-coupling calculations are prohibitive. Accordingly, parametric models of the relaxation matrix are often employed, ranging from very simple models to sophisticated schemes such as the energycorrected sudden (ECS) approximation.¹ The ECS approach¹⁰ includes the angular momentum coupling needed to handle interbranch mixing, and expresses the relaxation matrix (for an atomic perturber) in terms of a set of so-called "basic rates" $Q'_{I}(T)$, which are actually thermally averaged inelastic cross sections for downwards transitions to the ground state, $\sigma^0(L \rightarrow 0, T)$. In the past, the basic rates have usually been modeled through some simple analytical expression, such as the exponential power (EP) law,¹¹

$$Q'_{L}(T) = \frac{A(T)}{[L(L+1)]^{\alpha}} e^{-\beta(E_{L}/k_{B}T)}.$$
(1)

The adjustable parameters A, α , and β have usually been determined from measurements of quantities such as line-

widths, *Q*-branch profiles, and band wing absorptions through an ECS calculation. However, these "experimental" basic rates are quite strongly model-dependent, and it is of great interest to compare them with values of $Q'_L(T)$ calculated directly from a reliable intermolecular potential. Hutson *et al.*^{12,13} have recently developed such a potential for the system CO₂–Ar, and this gives us the opportunity to test the ECS approach for a relatively heavy system for which a large body of experimental results exists. This is the purpose of the present paper.

The present work may be justified in an alternative way. Since a reliable CO_2 -Ar surface now exists, the basic rates $Q'_L(T)$ are in principle known. Therefore there remains only *one* adjustable parameter in the ECS model, the scaling length l_c which appears in the adiabaticity factors discussed below. Is it still possible to obtain consistent agreement between ECS calculations and a wide variety of experimental data? In this sense, the present paper provides a more stringent test of the ECS approach than any of the previous studies¹⁴⁻¹⁸ which treated the $Q'_L(T)$ as adjustable.

The remainder of this paper is organized as follows. Section II gives a resume of the ECS formalism. Section III presents the results of CS calculations of the basic rates $Q'_L(T)$ from the accurate potential of Ref. 12. Section IV compares ECS pressure-broadened linewidths and synthetic profiles obtained from the calculated basic rates with experiment. Section V compares the calculated basic rates themselves with those previously deduced from experiment through analytical models [Eq. (1)]. Finally, Sec. VI gives some concluding remarks.

II. REVIEW OF THE ECS FORMALISM

A. Absorption coefficient

Within the impact approximation, the absorption coefficient including line-mixing effects is given by^{4,5,19,20}

$$\alpha(\sigma) = \frac{8\pi^2 \sigma}{3hc} n_{\rm CO_2} (1 - e^{-(hc\sigma/k_BT)}) \sum_{\substack{\text{vibrational}\\\text{band}}} |R_v|^2 \\ \times \mathrm{Im} \sum_{k,l} d_l \langle \langle l | (\sigma - \sigma_0 - in_{\rm Ar}^* W^0)^{-1} | k \rangle \rangle d_k \rho_k,$$
(2)

where n_{CO_2} is the number density of the absorbing species and n_{Ar}^* is the effective number density of the perturber, which takes excluded volume effects into account at high densities as explained in Ref. 15. The quantity d_k is the reduced dipole matrix element for line $|k\rangle$ $= |v_i j_i \epsilon_i, v_f j_f \epsilon_f \rangle$, where v_i and v_f each represent a complete set of vibrational quantum numbers $(v_1v_2l_2v_3)$, j is the rotational angular momentum quantum number, and ϵ is the parity index.^{20,21} The quantity ρ_k is the population of the initial level of line k, σ and σ_0 are diagonal matrices associated with the scanning wave number and the line positions, respectively, and R_v is the vibrational transition moment. The HITRAN-96 database²² for CO₂ provides line positions and line strengths for the line-mixing calculation.

The (complex) relaxation matrix $W \equiv n_{Ar}^* W^0$ exists in line space, with rows and columns labeled by spectroscopic transitions. Its diagonal elements are equal to the pressurebroadened widths and shifts for nonoverlapping lines. The matrix elements of *W* are expressed in terms of infrared mixing cross sections by

$$\langle \langle l | W | k \rangle \rangle = \frac{n_{\text{Ar}}^* \overline{v}}{2 \pi c} \, \sigma^1(l \leftarrow k), \tag{3}$$

where \overline{v} is the mean relative velocity. As shown by Green,^{20,21} the cross sections depend strongly on the values of the vibrational angular momentum l_2 (denoted *l* below) involved in the transitions. However, Green's calculations²¹ were limited by the infinite order sudden (IOS) approximation applied to the rotation.

B. Obtaining ECS cross sections

1. Real part

In the IOS approximation, the infrared line shape cross sections σ^1 are given by

where [X]=2X+1. The spectroscopic coefficients *F* are given by Eq. (3) of Ref. 20. However, this expression relies on a factorisation formula that expresses all the inelastic cross sections $\sigma^0(j \rightarrow j', E)$ in terms of $\sigma^0(0 \rightarrow L, E)$, and the factorization is valid only in the energy sudden approximation, where the internal energies of the colliding molecules are neglected. The ECS approach introduces "adiabaticity factors" Ω_J which approximately correct for the changes in kinetic energy and the finite duration of collisions.¹⁰ Two possible choices for the adiabaticity factors will be discussed below.

Two different ECS formalisms have been proposed for line shape calculations. In the approach of Ref. 20, adiabaticity corrections are applied directly to the line shape cross sections, and Eq. (4) is replaced by

$$\sigma_{j'_i j'_f j_i j_f}^{1l_i l_f} = -\left(\frac{[j'_i]}{[j_i]}\right)^{1/2} \sum_{L} [L] F_{j'_i j'_f j_i j_f}^{1l_i l_f L} \frac{\sqrt{\Omega_{j_i} \Omega_{j_f}}}{\Omega_L} Q'_L.$$
(5)

Detailed balance is enforced by using Eq. (5) only for downward cross sections $[j_i > j'_i]$, with upward ones obtained from

$$\sigma^{1}(l \leftarrow k)\rho_{k} = \sigma^{1}(k \leftarrow l)\rho_{l}.$$
(6)

Vibrational dephasing is assumed to be negligible, and the real parts of the diagonal elements (linewidths) are deduced from the rigid-rotor sum rule,²³

$$d_k \sigma^1(k \leftarrow k) = -\sum_{l \neq k} d_l \sigma^1(l \leftarrow k).$$
⁽⁷⁾

The second ECS formalism for line shapes, developed by the group in Besançon,^{17,18,24} also starts from Eq. (4). However, in this approach the tetradic (off-diagonal) coupling cross sections are *first* expressed, within the IOS limit, in terms of dyadic (diagonal) cross sections that depend on factors $1/\tau_j^{ll'}$ that appear in the formalism. These factors are deduced from a realistic description of the relaxation of **J**, the rotational angular momentum, and of higher-order tensors (J^2 , etc.) associated with **J**.

The approach of Ref. 24 leads to a formalism that appears at first sight to be completely different from that derived directly from the IOS model.²⁰ However, both approaches have successfully predicted the evolution of various CO_2 bands over an extended range of perturber densities.^{14–18} A recent series of papers, devoted to the analysis of line mixing effects in CO_2 –Ar (but using adjustable basic rates $Q'_L(T)$) has demonstrated that the two formalisms are mathematically identical when the approximation $\tau_j^{II} \cong \tau_j^{II'}$ is valid.¹⁸ For CO_2 –Ar this approximation is good¹⁸ and the model of Ref. 20—which is easier to handle—is physically justified. In the following, therefore, off-diagonal elements of W are calculated from Eqs. (5) and (6) and diagonal ones from the sum rule (7).

2. Imaginary parts

The ECS formalism does not provide the imaginary part of the relaxation matrix. Because of this, most researchers have chosen to set the imaginary parts of off-diagonal elements arbitrarily to zero (though the diagonal elements, which are the line shifts, are usually known experimentally). The imaginary part of W has only small effects in the low perturber density/weak overlapping regimes, but it cannot be neglected at high perturber pressures. In the present paper we wish to consider $\Sigma - \Sigma$ bands of CO₂ under high pressures of argon. We thus cannot afford to set the imaginary part to zero, and the model that we have used will be discussed below.

C. Two models of the adiabaticity factor

As discussed above, the IOS factorization formula is not very accurate for a system such as CO_2 -Ar, and corrections must be introduced to take account of the change in kinetic energy upon collision and the finite duration of collisions. For this purpose, De Pristo *et al.*¹⁰ have introduced an adiabaticity factor

$$\Omega_J^{\rm DP} = \left[1 + \omega_{JJ-2}^2 \frac{l_c^2}{24\bar{v}^2} \right]^{-2}, \tag{8}$$

where ω_{JJ-2} is the frequency spacing between adjacent coupled levels and l_c is a scaling length. This simple analytical form results from a second-order calculation of the correction to the IOS limit for an *S*-matrix element in terms of the "duration of collision" l_c/\bar{v} . However it has been shown that Eq. (8) may in some circumstances overestimate the adiabaticity factor and lead to unphysical behavior of the ECS model.²⁵ An alternative method has thus been proposed, based on approximating the square of the phase integral governing the inelasticity by a Padé approximant. The resulting expression for the adiabaticity factor is²⁵

$$\Omega_J^B = \left[1 + \omega_{JJ-2}^2 \frac{l_c^2}{12\bar{v}^2} \right]^{-1}.$$
(9)

We will refer to Eq. (8) as the "De Pristo" factor and Eq. (9) as the "Bonamy" factor. ECS calculations using these two models will be compared below.

III. COUPLED STATES CROSS SECTIONS

As mentioned previously, Hutson *et al.* have obtained two potential energy surfaces for CO₂–Ar, designated "single repulsion" and "split repulsion," by least-squares fitting of a parameterized functional form to the highresolution spectra of van der Waals complexes and the second virial coefficients of gas mixtures.¹³ The resulting potentials have been shown to reproduce experimental transport properties, NMR relaxation times, and pressure-broadened linewidths,¹² none of which was used in fitting the surfaces. In view of the similarity of the linewidth calculations for the two potentials, we have considered only the "single repulsion" potential in the present work.

Coupled-states (CS) inelastic cross sections $\sigma^0(j \rightarrow j', E)$ were first calculated, using the MOLSCAT program,²⁶ for a grid of total energies *E*. The results for upwards cross sections $\sigma^0(0 \rightarrow L, E) \equiv Q_L(E)$ are given in Table I. The basis set used included all rotor functions up to $j \cong 38$, which should give reasonable convergence for cross sections up to about $L \cong 30$.

The "downwards" cross sections $\sigma^0(L \rightarrow 0, E) \equiv Q'_L(E)$ from CS calculations automatically satisfy microscopic reversibility,²⁷

$$(E - E_L)(2L + 1)\sigma^0(L \to 0, E - E_L) = E\sigma^0(0 \to L, E),$$
(10)

where E_L is the internal energy of level *L*. The downwards cross-sections were averaged over kinetic energy $E_t = E$ $-E_L$ according to the Maxwell–Boltzmann distribution,

$$Q'_{L}(T) = \frac{1}{(kT)^{2}} \int_{0}^{\infty} E_{t} e^{-E_{t}/k_{B}T} Q'_{L}(E_{t}) dE_{t}$$
(11)

giving the thermally averaged basic rates $Q'_L(T)$ needed in the ECS model. Sample results, for T=296 K, are given in Table II.

IV. RESULTS OF THE ECS FORMALISM

A. Pressure broadening of infrared $\Sigma {-}\Sigma$ lines and near wing absorption

We consider first the pressure broadening in *P* and *R* branches of $\Sigma_u \leftarrow \Sigma_g$ infrared bands, for which extensive measurements are available.^{16,28} The simplest ECS calculation that can be performed using the CS basic rates is to include only the $Q'_L(T)$ values for $L \leq 30$, i.e., only those for which the CS calculations are believed to be converged; this is referred to as the "truncated" CS-ECS approach. Figure 1(a) compares the truncated CS-ECS linewidths with some of the experimental data and with recent *direct* CS calculations¹² (not based on the ECS approximation) using the single repulsion potential. It may be seen that the agreement is reasonable (within 10%) for low rotational lines, up

TABLE I. Coupled-states ''upward'' cross sections $\sigma^0(0 \rightarrow L, E)$, in Å², computed from the ''single repulsion'' potential of Ref. 12 as a function of collision kinetic energy in cm⁻¹.

	L											
Ε	2	4	6	8	10	12	14	16	18	20	22	24
20	63.734	22.464	5.803									
30	69.433	20.548	11.460	4.368								
50	64.177	16.066	15.333	8.628	6.827							
75	54.984	22.284	11.696	7.232	15.235	12.482						
100	46.118	23.035	7.301	7.171	11.132	17.563	10.771					
125	48.295	22.692	12.045	6.212	7.735	12.627	14.381	6.484				
175	43.705	19.715	12.496	7.061	4.702	8.429	13.531	12.064	5.526	1.022		
200	38.838	20.630	11.079	8.338	4.734	6.844	10.853	12.213	8.392	2.359	0.343	
300	32.120	19.018	10.012	10.422	6.860	4.193	4.617	6.657	8.918	7.730	5.154	2.506
400	31.393	14.657	11.237	10.78	6.425	3.946	3.472	4.016	5.442	6.421	6.296	4.554
600	27.126	13.580	12.756	8.434	4.530	3.144	2.975	3.381	3.952	4.283	4.538	4.119
800	25.059	15.420	11.544	6.216	3.627	3.266	3.288	3.455	3.487	3.457	3.341	3.404
1000	25.256	16.181	10.117	5.040	3.380	3.058	3.047	3.167	3.147	3.170	3.064	2.851
1200	26.061	16.473	8.833	4.252	3.075	2.940	3.096	2.941	2.941	2.909	2.750	2.607
1400	26.916	15.618	7.733	4.635	3.021	2.796	2.817	3.088	2.851	2.648	2.536	2.483
1600	27.477	14.657	6.742	4.159	3.390	3.027	2.840	2.847	2.861	2.688	2.452	2.348
1800	27.849	13.537	6.148	3.895	3.293	3.041	3.000	2.753	2.797	2.712	2.590	2.312
2000	27.931	12.499	5.564	3.646	3.439	3.027	2.860	2.755	2.648	2.728	2.597	2.432
2215.401	27.882	11.492	5.147	3.447	3.275	3.078	2.841	2.767	2.564	2.572	2.519	2.360

to about $|m| \cong 16$, but beyond that the truncated CS-ECS results begin to fall well below both experiment and direct calculations. The falloff reflects the lack of $Q'_L(T)$ rates for L>30, which are needed for a proper evaluation of the cross sections according to Eqs. (5)–(7). A similar conclusion is reached by considering the normalized absorption in the near wing of the $3\nu_3[00^03 \leftarrow 00^00]$ band; as may be seen in Fig. 1(b), the absorption predicted from the truncated subset of $Q'_L(T)$ with $L \leq 30$ is considerably too small.

It is thus necessary to extrapolate the $Q'_L(T)$ results from the CS calculations to higher *L*. Various different ways of carrying out the extrapolation could be envisaged. In the present work, we have chosen to use the exponential power law, Eq. (1), and to determine the parameters *A*, α , and β (together with the scaling length) from a simultaneous fit of the pressure-broadened linewidths and the near-wing absorption in the $3\nu_3$ band, as described in Ref. 30. The values of

TABLE II. Thermally averaged "downward" cross sections $Q'_L(T) \equiv \sigma^0(L \rightarrow 0, T)$ (in Å²) from CS calculations at T = 296 K.

L	$Q(L \rightarrow 0;T)$
2	7.0746
4	2.0115
6	0.9355
8	0.5703
10	0.3436
12	0.2878
14	0.2872
16	0.2758
18	0.2536
20	0.2118
22	0.2009
24	0.1524
26	0.1216
28	0.1089
30	0.0928



FIG. 1. (a) Comparison of calculated and experimental linewidths (halfwidths at half-maximum) for infrared $\Sigma - \Sigma$ band lines (T = 296 K). \bigcirc , experimental results of Ref. 29; \blacktriangle , CS theoretical results of Ref. 12, obtained from the "single repulsion" potential; ---, truncated CS-ECS results. The sum over *L* is limited to L = 30 and the "Bonamy" adiabaticity factor is used (with $l_c = 3.5$). (b) Normalized absorption (in cm⁻¹ amagat⁻²) in the wing of the $3\nu_3$ band at T = 296 K. \bigcirc , experimental results of Ref. 14, Rennes; \bigcirc , experimental results of Ref. 14, St Petersburg; --, truncated CS-ECS results. The sum over *L* is limited to L = 30 and the "Bonamy" adiabaticity factor is used (with $l_c = 3.5$).

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TABLE III. Extrapolated set of Q'_L basic rates. For $L \le 24$ the rates are those of Table II. For $L \ge 30$, they are given by Eq. (1) with parameters A, α , and β depending on the model of the adiabaticity factor (together with the scaling length l_c). The values for L=26 and 28 join the direct CS results of Table II to the extrapolated ($L \ge 30$) part of the Q'_L set.

		De Pristo adiabacity factor	Bonamy adiabacity factor
$L = \begin{cases} 26\\ 28 \end{cases}$		0.1216 0.1089	0.1153 0.0917
($A(\text{\AA}^2)$	36.74	6.142
<i>L</i> ≥30	lpha eta eta	0.89 0.02	0.6454 0.02
	$l_c(\text{\AA})$	2.0	3.5

 $Q'_L(T)$ for L < 26 are kept fixed at the CS values. The resulting parameters are given in Table III for both choices of adiabaticity factor. The ECS line shape model using these $Q'_L(T)$ values is referred to as the extrapolated CS-ECS model.

The linewidths from the extrapolated CS-ECS model are compared with the experimental results and with direct CS calculations in Fig. 2(a). It may be seen that including the extrapolated values has removed the artificial falloff in the CS-ECS results at high |m|. The two different models of the adiabaticity factor give substantially different results, and the factor of Bonamy *et al.*²⁵ gives better agreement with experiment and with direct calculations than that of De Pristo *et al.*¹⁰ This corroborates the previous analysis based on the N₂–N₂ case,²⁵ and in the remainder of this paper we will consider only results obtained with the "Bonamy" factor. The extrapolated CS-ECS predictions are also in good agreement with the experimental results for the normalized near wing absorption, as shown in Fig. 2(b).

The importance of the extrapolated part of the $Q'_L(T)$ cross sections may be emphasized by rewriting the absorption in the wing as

$$\alpha(\sigma) \propto \sum_{kl} \rho_k d_k d_l \frac{W_{lk}}{(\sigma - \sigma_k)(\sigma - \sigma_l)} \equiv \sum_{L \ge 2} P(\sigma, L) Q'_L.$$
(12)

The products ("weights") $P(\sigma,L) \times Q'_L$, for a characteristic wave number σ in the near wing of the $3\nu_3$ band, are shown in Fig. 3 as function of *L*. About 70% of the absorption arises from the extrapolated values. In other words, the near wing region is particularly well adapted for use in determining the "high-*L* tail" of the $Q'_L(T)$ set. Similarly, as may be seen in Fig. 4, a large part of the linewidths at high J_i comes from the high- $L Q'_L(T)$ rates.

By contrast, it must be emphasized that the linewidths at low J_i values ($J_i \le 16$) are sensitive only to low-*L* basic rates, i.e., to the $Q'_L(T)$ values obtained directly from the CS calculations. For these widths, the only adjustable parameter of the ECS formalism is the scaling length, and the agreement observed at low J_i in Figs. 1(a) and 2(a) provides a stringent test of the ECS formalism. It is thus worthwhile to



FIG. 2. (a) Comparison of calculated and experimental linewidths for infrared Σ - Σ band lines (T=296 K). \bigcirc , experimental results of Ref. 29; \bullet , experimental results of Refs. 16 and 28; \blacktriangle , direct CS results of Ref. 12, using the "single repulsion" potential; —, extrapolated CS-ECS calculation with the "Bonamy" adiabaticity factor; ---, extrapolated CS-ECS calculation with the "De Pristo" adiabaticity factor. The scaling lengths l_c and the extrapolated Q'_L rates are given in Table III. (The vertical bar indicates an absolute error of 5%.) (b) Normalized absorption in the wing of the $3\nu_3$ band at T=296 K. \bigcirc , experimental results of Ref. 14, Rennes; \bullet , experimental results of Ref. 14: St Petersburg; —, extrapolated CS-ECS calculation with the Bonamy adiabaticity factor. The scaling length and the extrapolated Q'_L rates are given in Table III.

test the ECS model against other properties that depend on line mixing and were not considered in the extrapolation of the basic rates.

B. Spectra at high perturber density

We next consider the evolution of the absorption spectrum in the central region of the $3\nu_3$ band for Ar pressures



FIG. 3. Partial contributions to the normalized absorption at σ =7010 cm⁻¹ in the wing of the 3 ν_3 band as a function of *L*.



FIG. 4. Comparison of directly calculated CS linewidths for infrared $\Sigma - \Sigma$ *P*-branch lines with ECS predictions. \blacktriangle , Direct CS results of Ref. 12; ---, truncated CS-ECS calculation. The sums over *L* are limited to *L*=30; --, extrapolated CS-ECS calculation. The extrapolated Q'_L rates are given in Table III.

up to about 1000 atm. Similar results have been obtained for the ν_3 band, but will not be reported here. The real part of the relaxation matrix is given by Eqs. (5)–(7) and the basic rates by Tables II and III. As mentioned above, for such high densities at least an approximate description of the imaginary part of the relaxation matrix is essential. A suitable model has been proposed and discussed in Ref. 18. The result is

$$\langle \langle P(J) | \operatorname{Im} W | P(J') \rangle \rangle = (-\Delta_v + \Delta_R) \, \delta_{JJ'},$$

$$\langle \langle R(J) | \operatorname{Im} W | R(J') \rangle \rangle = (-\Delta_v - \Delta_R) \, \delta_{JJ'},$$

$$\langle \langle P(J) | \operatorname{Im} W | R(J') \rangle \rangle = \Delta_R \, \delta_{JJ'},$$

$$\langle \langle R(J) | \operatorname{Im} W | P(J') \rangle \rangle = -\Delta_R \, \delta_{JJ'}.$$

$$(13)$$

The imaginary part of W thus depend on two parameters Δ_v and Δ_R . Δ_v is an overall pressure shift of the band, mainly due to vibrational dephasing. It may be noted that, if vibrational dephasing has no influence on the real part of the sum rule [Eq. (7)], the converse is true for the imaginary part. In the present work, Δ_v has been fixed at the value determined previously,¹⁸ $\Delta_v = -17.1 \times 10^{-3} \text{ cm}^{-1} \text{ amagat}^{-1}$. Δ_R is a differential shift of the P and R branches with respect to the band center. Following Ref. 18, we consider it to be an adjustable parameter and determine it from the comparison between experiment and theory for various perturber densities. The linearity of the curve of Δ_R against effective perturber density n_{Ar}^* is a further test whether Im W is being modeled realistically. As in Ref. 18, the curve obtained here is very nearly linear, and the value obtained is $\Delta_R = -6.8 \times 10^{-3} \text{ cm}^{-1} \text{ amagat}^{-1}$, which is very close to that obtained previously¹⁸ ($\Delta_R = -7.\times 10^{-3} \text{ cm}^{-1} \text{ amagat}^{-1}$). The quality of the extrapolated CS-ECS results is illustrated in Figs. 5(a)-5(c). It may be seen that the extrapolated CS-ECS model gives an accurate description of the band profile for a very wide range of perturber densities.

C. Infrared Q branches

Previous work has demonstrated the effects of the parity of the rotational states and of the vibrational angular momentum on the shape of Q branches.^{17,20,21} Cross sections coupling P, Q, and R-branch lines may be calculated from Eq.



FIG. 5. Absorption coefficient in the central region of the $3\nu_3$ band. \bullet , experimental results of Ref. 15; —, extrapolated CS-ECS results; (a) $n_{\rm CO_2}$ =3.25 Am, $n_{\rm Ar}$ =144.6 Am, $n_{\rm Ar}^*$ =160.1 Am; (b) $n_{\rm CO_2}$ =3.25 Am, $n_{\rm Ar}$ =283.1 Am, $n_{\rm Ar}^*$ =345.2 Am; (c) $n_{\rm CO_2}$ =3.26 Am, $n_{\rm Ar}$ =545.5 Am, $n_{\rm Ar}^*$ =765.6 Am. ---, Lorentzian calculation (without any line mixing).

(5) for CO₂ vibrational bands of any symmetry.²⁰ ECS calculations have previously been shown to give good results for infrared and Raman spectra under a wide range of physical conditions (temperature, perturber density, nature of the perturber, band symmetry, etc.), but all the earlier studies^{16,17,20} used adjustable rates $Q'_L(T)$. For CO₂-Ar, knowledge of the most important rates from direct CS calculations allows us to carry out a more stringent test of the ECS formalism. Some typical results from the extrapolated CS-ECS procedure are compared with experimental profiles in Figs. 6–8. Once again the agreement is good, whatever the symmetry of the vibrational band considered. It has been shown in Ref. 17 that the evolution of $Q'_L(T)$ with *L* governs the amount of intrabranch coupling and thus the *Q*-branch line shape. In the present work, the *L* dependence is not



FIG. 6. Absorption in two *Q* branches of $\Sigma \leftarrow \Pi$ symmetry (*T*=305 K). •, experimental results of Ref. 17; —, extrapolated CS-ECS results; ---, Lorentzian calculation neglecting line mixing. (a) (10°0)_{II} \leftarrow 01¹0 band; n_{CO_2} =0.042 Am, n_{Ar} =10.3 Am. (b) (10°0)_I \leftarrow 01¹0 band; n_{CO_2} =0.025 Am, n_{Ar} =5.03 Am.

adjustable, so that the agreement obtained here confirms the accuracy of both the CS-ECS formalism and the CO_2 -Ar potential energy surface.

V. TEST OF THE PREVIOUS DETERMINATIONS OF THE Q_L RATES

All previous ECS calculations assumed that the basic rates $Q'_L(T)$ may be expressed through a simple analytical



FIG. 8. Absorption in a *Q* branches of $\Delta \leftarrow \Pi$ symmetry, $(12^{2}0)_{I} \leftarrow 01^{1}0$ band (*T*=296 K). •, experimental results of Ref. 29; —, extrapolated CS-ECS results; ---, Lorentzian calculation without line mixing. $n_{CO_{7}}=4.9 \times 10^{-2}$ Am, $n_{Ar}=2.2$ Am.

law such as Eq. (1), characterized by parameters determined from fitting experimental data. The present work provides independent basic rates for low L based on a reliable potential, and thus gives us the opportunity to check the "inversion method" used previously.

The directly calculated $Q'_{I}(T)$ values, from thermal averaging of CS cross sections calculated on the single repulsion potential, are compared in Fig. 9 with some sets of values determined previously using an ECS formalism and Eq. (1). The results are not so bad. The agreement is mostly within $\pm 20\%$ over a range where the $Q'_L(T)$ themselves vary by two orders of magnitude. Of course, an inversion based on a simple law such as Eq. (1) cannot reproduce the fine details of the rotational dependence of the $Q'_L(T)$ and some oscillations that arise from this may be seen in Fig. 9. Nevertheless, the comparison validates to some extent all the previous ECS-based work devoted to the CO₂-Ar system and makes it unnecessary to repeat the detailed analyses of the sensitivity of line shape calculations to such things as the L-dependence of the $Q'_{L}(T)$, the type of vibrational band involved, and the physical conditions under which the data were obtained.



FIG. 7. Absorption in a *Q* branch of $\Pi \leftarrow \Sigma$ symmetry; $01^{1}0 \leftarrow 00^{0}0$ band (*T*=296 K). •, experimental results (details can be found in Ref. 31); —, extrapolated CS-ECS results; ---, Lorentzian calculation without line mixing; $n_{CO_{2}}=6.110^{-3}$ Am, $n_{Ar}=18.5$ Am.



FIG. 9. Comparison of calculated CS cross sections Q'_L (from the single repulsion potential of Ref. 12; cf. Table II) with sets of Q'_L obtained from fitting of various data through an ECS formalism and Eq. (1); \bullet , optimized values of Ref. 17; \bigcirc , optimized values of Ref. 16.

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VI. CONCLUSIONS

We have computed inelastic cross sections for CO₂-Ar, using coupled-states (CS) calculations on the intermolecular potential of Hutson *et al.*, 12,13 and have used these to calculate the "basic rates" $Q'_L(T)$ that appear in the energycorrected sudden (ECS) model of line shapes. We have then used these to check the accuracy of the ECS approach by calculating infrared linewidth cross sections. The ECS calculations at low J_i values ($J_i \leq 16$) depend only on the low-L basic rates, for which the CS calculations are converged. For line shape calculations at higher J_i , basic rates for higher L are needed and an extrapolation procedure has been used. The resulting model, designated the extrapolated CS-ECS procedure, performs well for high-pressure band profiles (up to 1000 atm) and for near-wing absorption as well as for linewidths. The adiabaticity factor recently proposed by Bonamy et al.²⁵ appears to perform better than that of De Pristo *et al.*¹⁰ Finally, the CS basic rates have been used to evaluate the accuracy of the empirical basic rates $Q'_{I}(T)$ obtained previously from an optimization procedure based on a simple analytical law.

This work has shown how to take one step towards a more sophisticated calculation of the relaxation operator. The extrapolated CS-ECS procedure introduced here should be of general utility in calculating band profiles and other quantities from scattering calculations, which always use limited basis sets. As the next step, it would be very interesting to undertake a direct calculation of the relaxation matrix W, or at least of its major elements, using the coupledstates approximation. A reliable potential is available for CO₂-Ar, and such calculations are feasible with current computational abilities. However it must be remembered that even such a direct calculation would be limited by the impact approximation, which replaces all off-energy-shell transition matrices by on-shell counterparts. The resulting relaxation matrix then no longer satisfies detailed balance, 32,33 Eq. (6), and the sum rule, Eq. (7). Moreover, it leads to spurious results for the imaginary part of W,³³ which is of some importance in the calculation of the line shape at high perturber density. It is known that the impact approximation does not give a good description of the far wings of lines or of the coupling between very distant lines.^{33,34}

The theory of line shapes remains nontrivial, and many aspects of it are still not well understood. However, since a reliable potential now exists for CO_2 –Ar, it is a good candidate for calculations to investigate fundamental issues such the adequacy of the Fano–Ben Reuven formalism and the importance of off-shell molecular scattering calculations.³⁵

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