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Energy corrected sudden calculations of linewidths and line shapes based on coupled states cross sections: The test case of CO\textsubscript{2}–argon

F. Thibault, J. Boissoles, C. Boulet, L. Ozanne, J. P. Bouanich, C. F. Roche, and J. M. Hutson

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Line shape, transport and relaxation properties from intermolecular potential energy surfaces: The test case of CO\textsubscript{2}–Ar
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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The accuracy of the energy-corrected sudden (ECS) formalism for line shape calculations is investigated, using coupled states calculation for CO$_2$–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 $\sigma(L\rightarrow 0,E)=Q_j^L(E)$ are calculated using the MOLSCAT program, and then averaged over Maxwell–Boltzmann kinetic energy distributions to give the thermally averaged “basic rates” $Q_j^L(T)$ 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.

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. 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. 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. 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 method or a variety of quantum approximations 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. 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 energy-corrected sudden (ECS) approximation. The ECS approach 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” $Q_j^L(T)$, which are actually thermally averaged inelastic cross sections for downwards transitions to the ground state, $\sigma(L\rightarrow 0,T)$. In the past, the basic rates have usually been modeled through some simple analytical expression, such as the exponential power (EP) law,

$$Q_j^L(T) = \frac{A(T)}{[L(L+1)]^{\alpha}} e^{-\beta L/E_L/k_B T},$$

(1)

where $Q_j^L(T)$ is the line shape function, $A(T)$ and $\alpha$, and $\beta$ 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.\textsuperscript{12,13} have recently developed such a potential for the system CO$_2$–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 studies\textsuperscript{14–18} which treated the ECS pressure-broadened linewidths and synthetic line shapes.

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 line shapes 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\textsuperscript{4,5,19,20}

$$\tilde{\alpha}(\sigma) = \frac{8\pi^2 \sigma}{3\hbar c} n_{\text{CO}_2}(1 - e^{-(\hbar c\sigma/k_B T)}) \sum_{\text{vibrational band}} |R_v|^2 \times \text{Im} \sum_{k,l} d_{k,l}(\langle l|\sigma - \sigma_0 - in_{\text{Ar}W^0}^{-1}|k\rangle) d_k \rho_k,$$

where $n_{\text{CO}_2}$ is the number density of the absorbing species and $n_{\text{Ar}}^*$ 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 $d_{k,l}$ is the reduced dipole matrix element for line $|k\rangle$ = $|v_i,j_i\epsilon_i,v_j,j\epsilon_j\rangle$, where $v_i$ and $v_j$ each represent a complete set of vibrational quantum numbers $(v_i,v_j,j_3,j_2,j_1)$, $j$ is the rotational angular momentum quantum number, and $\epsilon$ is the parity index.\textsuperscript{20,21} The quantity $\rho_k$ is the population of the initial level of line $k$, $\sigma$ and $\sigma_0$ 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 database\textsuperscript{22} for CO$_2$ provides line positions and line strengths for the line-mixing calculation.

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

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

where $\nu$ is the mean relative velocity. As shown by Green,\textsuperscript{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 calculations\textsuperscript{21} 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 $\sigma^1$ are given by

$$\text{IOS} \sigma^1(l\rightarrow k) = \text{IOS} F^0_{j_f,j_i L} Q'_L,$$

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” $\Omega_L$ which approximately correct for the changes in kinetic energy and the finite duration of collisions.\textsuperscript{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

$$\sigma^1_{j_f,j_i L} = \left(\frac{\Omega_{j_f}}{\Omega_{j_i}}\right)^{1/2} \sum_L [L] F^0_{j_f,j_i L} Q'_L.$$

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

$$\sigma^1(l\rightarrow k) \rho_k = \sigma^1(k\rightarrow l) \rho_l.$$

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

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

The second ECS formalism for line shapes, developed by the group in Besançon,\textsuperscript{17,18,24} also starts from Eq. (4). However, in this approach the tetradic (off-diagonal) cou-
pling cross sections are first expressed, within the IOS limit, in terms of dyadic (diagonal) cross sections that depend on factors $1/l_{W}^{2j}$ 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. However, both approaches have successfully predicted the evolution of various CO$_2$ bands over an extended range of perturber densities. 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 $T''/T''\equiv r''/r''$ is valid. For CO$_2$–Ar this approximation is good 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 Σ–Σ bands of CO$_2$ 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. have introduced an adiabaticity factor

$$\Omega_J^{DP} = \left[1 + \omega_{jj-2}^2 \frac{l_c^2}{2v^2}\right]^{-1}, \quad (8)$$

where $\omega_{jj-2}$ 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 the S-Matrix element in terms of the ‘‘duration of collision’’ $l_c/v$. 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. 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 is

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

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 CO$_2$–Ar, designated ‘‘single repulsion’’ and ‘‘split repulsion,’’ by least-squares fitting of a parameterized functional form to the high-resolution spectra of van der Waals complexes and the second virial coefficients of gas mixtures. The resulting potentials have been shown to reproduce experimental transport properties, NMR relaxation times, and pressure-broadened linewidths, 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, for a grid of total energies $E$. The results for upwards cross sections $\sigma^0(0 \rightarrow L,E) = Q_L(E)$ are given in Table I. The basis set used included all rotor functions up to $j \equiv 38$, which should give reasonable convergence for cross sections up to about $L \equiv 30$.

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

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

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

$$Q'_L(T) = \frac{1}{(kT)^{3/2}} \int_0^\infty E_i e^{-E_i/kT}Q'_L(E_i)dE_i, \quad (11)$$

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 Σ–Σ lines and near wing absorption

We consider first the pressure broadening in $P$ and $R$ branches of Σ$_u$–Σ$_g$ infrared bands, for which extensive measurements are available. 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 calculations (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
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TABLE I. Coupled-states “upward” cross sections $\sigma^u(0\rightarrow L,E)$, in Å², computed from the “single repulsion” potential of Ref. 12 as a function of collision kinetic energy in cm$^{-1}$.

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<th>2</th>
<th>4</th>
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<td>10.771</td>
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TABLE II. Thermally averaged “downward” cross sections $\sigma^d(L\rightarrow 0,T)$ (in Å²) from CS calculations at $T=296$ K.

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<tr>
<td>26</td>
<td>0.1216</td>
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<tr>
<td>28</td>
<td>0.1089</td>
</tr>
<tr>
<td>30</td>
<td>0.0928</td>
</tr>
</tbody>
</table>

FIG. 1. (a) Comparison of calculated and experimental linewidths (half-widths at half-maximum) for infrared $\Sigma-\Sigma$ band lines ($T=296$ K). $\bigcirc$, experimental results of Ref. 29; $\bullet$, CS theoretical results of Ref. 12, obtained from the “single repulsion” potential; $\cdots\cdots$, 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; $\bullet$, 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 $l_c=3.5$).

to about $|m|=16$, but beyond that the truncated CS-ECS results begin to fall well below both experiment and direct calculations. The falloff reflects the lack of $Q^d_L(T)$ 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 $3\nu_3(000\rightarrow 000)$ band; as may be seen in Fig. 1(b), the absorption predicted from the truncated subset of $Q^d_L(T)$ with $L\leq30$ is considerably too small.

It is thus necessary to extrapolate the $Q^d_L(T)$ 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 $A$, $a$, and $b$ (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 III. Extrapolated set of $Q'_L$ basic rates. For $L \leq 24$ the rates are those of Table II. For $L \geq 30$, they are given by Eq. (1) with parameters $A$, $\alpha$, and $\beta$ 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 ($L \geq 30$) part of the $Q'_L$ set.

<table>
<thead>
<tr>
<th>$L$</th>
<th>De Pristo adiabicity factor</th>
<th>Bonamy adiabicity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.1216</td>
<td>0.1153</td>
</tr>
<tr>
<td>28</td>
<td>0.1089</td>
<td>0.0917</td>
</tr>
<tr>
<td>$A(\text{Å}^2)$</td>
<td>36.74</td>
<td>6.142</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.89</td>
<td>0.6454</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$l_c(\text{Å})$</td>
<td>2.0</td>
<td>3.5</td>
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</table>

$Q'_L(T)$ 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. gives better agreement with experiment and with direct calculations than that of De Pristo et al. This corroborates the previous analysis based on the $N_2-N_2$ case, 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 of the wing may be emphasized by rewriting the absorption in the wing as

$$\alpha(\sigma) \propto \sum_{kL} \rho_{rkd_kd_l} \frac{W_{kl}}{(\sigma - \sigma_k)(\sigma - \sigma_l)} = \sum_{L \geq 2} P(\sigma, L)Q'_L.$$

The products (‘‘weights’’) $P(\sigma, L) \times Q'_L$, for a characteristic wave number $\sigma$ 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 ($J_i \approx 16$) 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 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. 2. (a) Comparison of calculated and experimental linewidths for infrared $\Sigma-\Sigma$ band lines ($T = 296$ K). $\bigcirc$, experimental results of Ref. 29; $\bullet$, experimental results of Refs. 16 and 28; $\Delta$, 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.

FIG. 3. Partial contributions to the normalized absorption at $\sigma=7010$ cm$^{-1}$ in the wing of the $3 \nu_3$ band as a function of $L$.  

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up to about 1000 atm. Similar results have been obtained for the $v_3$ 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

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

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

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

$$\langle\langle R(J)|\text{Im } W|P(J')\rangle\rangle = -\Delta_R\delta_{JJ'}.$$ (13)

The imaginary part of $W$ thus depend on two parameters $\Delta_v$ and $\Delta_R$. $\Delta_v$ 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, $\Delta_v$ has been fixed at the value determined previously,$^{18}$ $\Delta_v = -17.1 \times 10^{-3}$ cm$^{-1}$ amagat$^{-1}$. $\Delta_R$ 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 $\Delta_R$ 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 $\Delta_R = -6.8 \times 10^{-3}$ cm$^{-1}$ amagat$^{-1}$, which is very close to that obtained previously$^{18}$ ($\Delta_R = -7.1 \times 10^{-3}$ cm$^{-1}$ 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. (5) for $CO_2$ 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 $CO_2$–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. 4. Comparison of directly calculated CS linewidths for infrared $\Sigma-\Sigma$ P-branch lines with ECS predictions. ▲, 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.](image)

![FIG. 5. Absorption coefficient in the central region of the $3v_3$ band. ●, experimental results of Ref. 15; ---, extrapolated CS-ECS results; (a) $n_{CO_2}=3.25$ Am, $n_{Ar}=144.6$ Am, $n^*_Ar=160.1$ Am; (b) $n_{CO_2}=3.25$ Am, $n_{Ar}=283.1$ Am, $n^*_Ar=345.2$ Am; (c) $n_{CO_2}=3.26$ Am, $n_{Ar}=545.5$ Am, $n^*_Ar=765.6$ Am. ---, Lorentzian calculation (without any line mixing).](image)
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 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 $Q_L(T)$ 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 ±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 CO$_2$–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.
VI. CONCLUSIONS

We have computed inelastic cross sections for CO$_2$–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” $Q^j_k(T)$ that appear in the energy-corrected 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 $J_1$ values ($J_1 \leq 16$) depend only on the low-$L$ basic rates, for which the CS calculations are converged. For line shape calculations at higher $J_1$, 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 $Q^j_k(T)$ 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 coupled-states approximation. A reliable potential is available for CO$_2$–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 as the adequacy of the Fano–Ben Reuven formalism and the importance of off-shell molecular scattering calculations.$^{35}$