Comparison of an *ab initio* calculation of the CO-Ar P(2) line shape with high-resolution measurements

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Abstract. A practical matrix-based formalism for solving the master equation for a spectral line is applied to the P(2) transition in the fundamental band of carbon monoxide perturbed by argon. The method assumes that the effect of intermolecular collisions on the internal relaxation of the molecules is uncorrelated with the effect of those collisions on the translational motion of the molecules. Comparison with high-resolution line shape measurements reveals that at low pressures, the omission of statistical correlation leads to a miscalculation of the shape of the line.

INTRODUCTION

A master transport-relaxation equation for the shape of a spectral line was presented as equation (10) in [1], and a theoretical formalism for solving that equation to calculate real line profiles was presented in [2] and [3]. That formalism is applied here to the case of the P(2) line of carbon monoxide perturbed by argon in an attempt to make – for the first time to our knowledge – accurate calculations of an isolated spectral line at all densities. In order to make the calculation more tractable, one key simplifying assumption is made: it is assumed that the effect of intermolecular collisions on the internal relaxation of the molecules is statistically uncorrelated with the effect of those collisions on the translational motion of the molecules. The calculations are then compared to high-resolution experimental data obtained recently by [4].

COLLISIONAL BROADENING

Because the internal and external degrees of freedom are assumed to be uncorrelated, it is possible to assume a different potential energy surface for each. The starting point for the calculation of the speed-dependent collisional broadening (i.e. the internal relaxation) is the potential energy surface of [5]. From there, fully quantal close coupled calculations of the broadening coefficient have been carried out using MOLSCAT and MOLCOL codes at the Université de Rennes. The dependence of the broadening coefficient on the relative molecular velocity can be fitted to an analytic function, which is then used to analytically determine the dependence of the broadening coefficient on the velocity of the active molecule. A dephasing collision matrix, $\mathbf{S}_D^f$, is then determined using equation (11) of [3].

DOPPLER BROADENING AND DICKE NARROWING

The potential energy surface used for determining the translational motion is that of a rigid sphere. The Doppler broadening is represented by the matrix $\mathbf{K}$, while the effect of Dicke narrowing is represented by the velocity changing collision matrix, $\mathbf{S}_{VC}^f$, as determined for the rigid sphere potential in [3].

MATRIX CALCULATIONS

As shown in [3], the line shape can now be determined from

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} c_0(\omega) ,$$

where $c_0(\omega)$ is the first element of the matrix $\mathbf{c}(\omega)$, and

$$\mathbf{b} = \mathbf{L}(\omega)\mathbf{c}(\omega) .$$

Here, $\mathbf{b}$ is a column matrix whose n^{th} element is $\delta_{n,0}$, and $\mathbf{L}(\omega)$ is given by

$$\mathbf{L}(\omega) = -i(\omega - \omega_0)\mathbf{1} + i\mathbf{K} - \mathbf{S}_D^f - \mathbf{S}_{VC}^f .$$

The size of these matrices is determined by the number of basis functions required to give the accuracy desired for the solution. In our case, it is always sufficient to use 121 basis functions. At higher pressures, only 36 basis functions are required.

COMPARISON WITH EXPERIMENTAL DATA

In the equation for the broadening coefficient as a function of the velocity of the active molecule, the half-width at half-maximum of the spectral line, Γ_0, appears as a multiplicative scaling factor. We are only able to calculate Γ_0 to an accuracy of 2%. We are able, however, to fit Γ_0 to an accuracy of 0.1% using the experimentally measured data. Since we are presently interested in testing our understanding of the physics and not in testing our ability to calculate Γ_0 precisely, we have chosen to fit Γ_0; that is, to determine it from a least squares minimization of the difference between our calculated and measured profiles.

At high densities, when the pressure is greater than about 0.2 atmospheres, the calculations agree with the measurements within the experimental noise. As the measurements were recorded with a signal-to-noise ratio of 3000:1 and a frequency resolution of 1.5 MHz, the calculations can be termed highly accurate.

As the pressure decreases below 0.2 atm, increasing disagreement is observed, as seen in the residuals plotted in Figure 1. Also shown is the result of removing Dicke narrowing from the calculations, which universally improves the agreement. The resulting profile is a speed-dependent Voigt profile (SDVP).

Figure 2 shows the behaviour of the fitted $\gamma_0 = \Gamma_0/P$ as a function of pressure. At high pressures, γ_0 is constant and within 1% of the calculated value, as should be expected. However, at lower pressures, γ_0 diverges, increasing drastically for our *ab initio* profile and decreasing slightly for the simplified SDVP. This picture is consistent with over-calculated Dicke narrowing in our *ab initio* profile and under-calculated Dicke narrowing (in fact, no Dicke narrowing at all) in the SDVP, for which the least squares minimization attempts to compensate by altering the overall half-width, Γ_0. The residuals in Figure 1 attest that altering the fitted Γ_0, even by these extreme amounts, is not capable of producing agreement between the calculated and measured profiles. This fact serves as an *a posteriori* justification for fitting Γ_0 in the first place.

There are two chief suspects in the failure of the *ab initio* calculation to reproduce real spectral profiles at low densities. The first is our choice of rigid spheres for the modelling of the translational motion. However, calculations have also been carried out using the speed-dependent Nelkin-Ghatak hard collision profile (SDNGP) [6] and the speed-dependent Galatry soft collision profile (SDGP) [7], and the same pattern of disagreement is observed, as shown in Figure 2. The interactions used in these two profiles are generally considered to be opposite, extreme cases, with most other models falling somewhere in between. Thus our results are not sensitive to our choice of interaction for the translational motion.

The second suspect is the assumption that the internal and external degrees of freedom are statistically uncorrelated. In fact, it seems likely that this assumption is the cause of the disagreement for two reasons. First, the CO-Ar system under study is known to be dominated by inelastic collisions, which by their definition involve a direct coupling between the internal and external degrees of freedom of the molecules. The second reason is that in a purely theoretical model proposed by [8] to account for
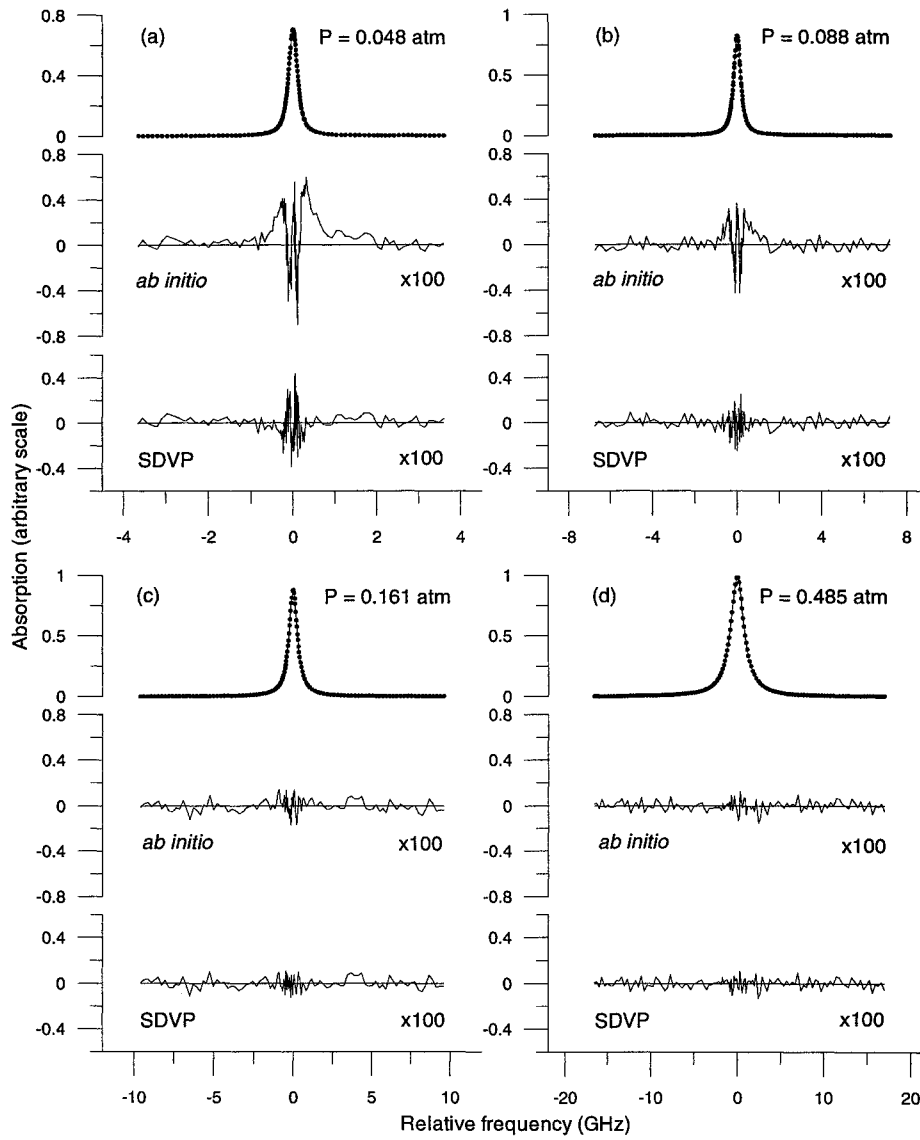
FIGURE 1. Line absorption profiles and residuals for the *ab initio* and speed-dependent Voigt (SDVP) profiles. Residuals are the calculated profile minus the measured profile, and are magnified 100 times. Four different pressures are shown in panels (a) – (d).
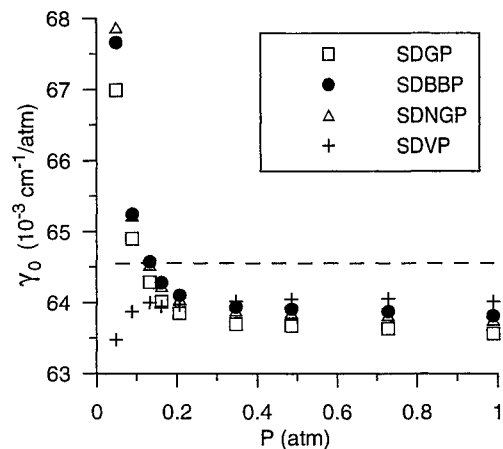
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FIGURE 2. Fitted broadening coefficients versus pressure for the *ab initio* speed-dependent billiard ball profile (SDBBP), speed-dependent Galatry profile (SDGP), speed-dependent Nelkin-Ghatak profile (SDNGP), and speed-dependent Voigt profile (SDVP). The calculated value with only 2% accuracy is shown as a dashed line.

statistical correlation, the effect of including the correlation was to reduce the amount of Dicke narrowing, which is consistent with the results of these *ab initio* calculations.

CONCLUSION

It will be necessary to perform a fully correlated calculation in order to generate accurate line shapes *ab initio* at all densities for the CO-Ar P(2) line. Omission of statistical correlation between the effects of collisions on the internal relaxation and external motion of the molecules results in an apparent reduction in Dicke narrowing. This reduction is not evident at high densities, but is manifested at low densities, where Doppler broadening and Dicke narrowing dominate the spectral line shape.

REFERENCES

1. May, A. D. *Phys. Rev. A* **59**, 3495-3505 (1999).
2. Shapiro, D. A., Ciurylo, R., Drummond, J. R., and May, A. D. *Phys. Rev. A* **65**, 012501 (2001).
3. Ciurylo, R., Shapiro, D. A., Drummond, J. R., and May, A. D. *Phys. Rev. A* **65**, 012502 (2001).
4. Berman, R., Sinclair, P. M., May, A. D., and Drummond, J. R. *J. Mol. Spec.* **198**, 283-290 (1999).
5. Tockzylowski, R. R. and Cybulski, S. M. *J. Chem. Phys.* **112**, 4604-4612 (2000).
6. Nelkin, M. and Ghatak, A. *Phys. Rev.* **135**, A4-9 (1964).
7. Galatry, L. *Phys. Rev.* **122**, 1218-1223 (1961).
8. Rautian, S. G. and Sobelman, I. I. *Usp. Fiz. Naut.* **90**, 209-236 (1966), *Trans. In Sov. Phys. Usp.* **9**, 701-716 (1967).