Calculations of rotational linewidths in HCl perturbed by argon

E. W. Smith*

Laser Physics Section, National Bureau of Standards, Boulder, Colorado 80302

M. Giraud

Université de Provence, Marseille, Cedex 4, France

(Received 28 October 1976)

In a previous paper[1] a new theory was presented for calculating the broadening of rotational lines in linear molecules perturbed by atoms. In that theory there were no adjustable parameters (such as impact parameter cutoffs etc.) because realistic curved trajectories were used for the motion of the nuclei and the S-matrix was evaluated to all orders in the atom–molecule interaction (rather than the usual perturbative approach). Comparisons were made with other theories including close coupling calculations, fully classical calculations and other semiclassical theories in order to demonstrate the validity of this new theory.

Having thus explored the validity and accuracy of the theory, calculations were made using recently developed atom–molecule potential surfaces[2] based on the Gordon-Kim electron gas model.[3] These theoretical potential surfaces also have no adjustable parameters

The Journal of Chemical Physics, Vol. 66, No. 4, 15 February 1977

yet they differ markedly from semiempirical potentials because they have strong contributions from very high order anisotropies. To show this, the atom–molecule interaction is expanded in terms of Legendre polynomials where r is the distance between the atom and the molecular center of mass and θ denotes the angle between this atom-molecule axis and the molecular axis itself [cf. Eqs. (2.1), (2.7), and (2.8) of Ref. (1)]:

$$V(r,\ \theta) = V_0(r) + \sum_l P_l(\cos\theta)\, V_l(r). \tag{1}$$

It is found that the theoretically determined potentials have large contributions from terms as high as V_6 or V_8 whereas semiempirical potentials usually contain only V_1 and V_2 anisotropies. For this reason it is sometimes said that the theoretical potentials are incorrect. However, our calculations of rotational line widths for CO_2 perturbed by Ar and He gave excellent agreement with experimental data ranging from very low to very high rotational states [i.e., from $J=3$ to $J=40$, see Figs. 5 and 6 of Ref. 1]. We believe that this is the first time a molecular line broadening theory *with no adjustable parameters*, using a purely theoretical potential surface, has obtained good agreement with experiment for such a wide range of quantum numbers. While these results were very encouraging, the agreement in the case of CO_2–Ar was not perfect, probably due to the influence of vibrational effects which were not included (see discussion in Sect. 6D of Ref. 1).

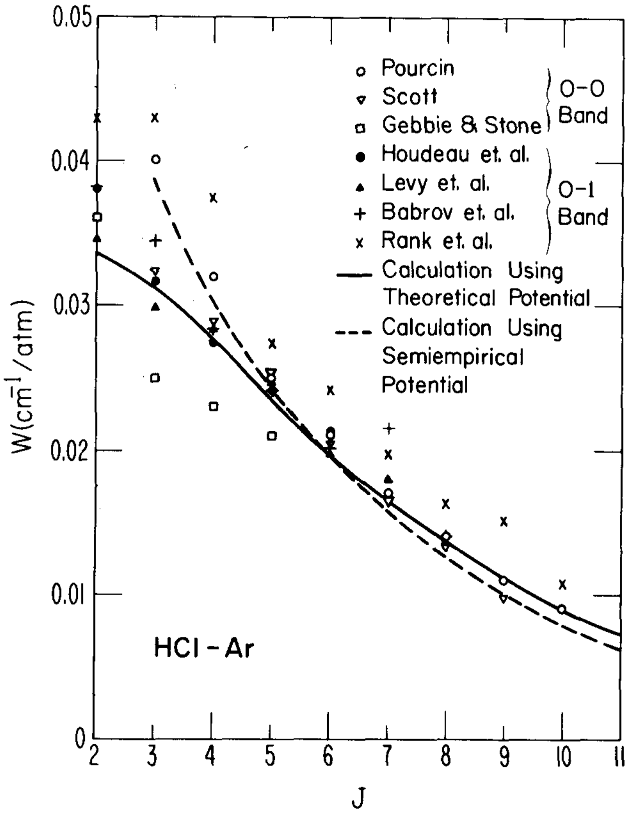

FIG. 1. Half widths in cm^{-1}/atm for the $J \rightarrow J$-1 rotational lines in the 0-0 and 0-1 vibrational bands of HCl perturbed by Argon as a function of J. The experimental data of Scott,[7] Pourcin,[8] Gebbie and Stone,[9] Levy *et al.*,[10] Houdeau *et al.*,[11] Babrov *et al.*,[12] and Rank *et al.*[13] are plotted with our calculations using the purely theoretical potential of Stevens and Robert[4] and the semiempirical potential of Neilsen and Gordon.[5] Note that the data of Scott were plotted incorrectly in Fig. 2 of Ref. 1.

We have therefore performed further calculations for HCl perturbed by Ar using a theoretical potential surface (again based on the Gordon-Kim model) recently developed by Stevens and Robert.[4] In these calculations we studied the relative importance of the various orders of anisotropies and found, as in the cases of CO_2–Ar, He (see Figs. 5 and 6 of Ref. 1), that terms up to V_4 were very important, V_5 and V_6 made contributions the order of 10% to the half widths, while the V_7 and V_8 terms produced 2% contributions. The S-matrix calculations employed the terms K_1, K_2, and K_3 (see Eqs. 4.15 and 4.16 of Ref. 1) but the K_3 term made only a 2% contribution to the half width as predicted in Sect. 6A of Ref. 1. The result of the complete calculation, including all terms up to V_8, is shown as the solid curve in Fig. 1.

For comparison we have also performed calculations using the best available semiempirical potential due to Neilsen and Gordon[5] (we used their $NC=52$ potential as discussed in Sect. 6B of Ref. 1). This potential again differs significantly from the purely theoretical potential of Stevens and Robert[4] in that the latter contains anisotropic terms as high as V_{10} whereas the semiempirical potential contains only V_1 and V_2. This calculation is shown as the dashed curve in Fig. 1.

The agreement between the two theoretical curves is very significant because the potentials employed are so dissimilar. This clearly shows that it is not possible to deduce a potential function from a set of line broadening measurements alone since the line width is not sufficiently sensitive to the details of the anisotropies. A detailed analysis of inelastic cross sections,[6] in conjunction with line broadening data, may provide a more sensitive probe for the potentials. We point out again (as in Ref. 1) that agreement between theory and experiment proves very little if one uses a semiempirical potential because the latter is derived from the experimental data by adjustment of its parameters. On the other hand, the excellent agreement with experiment obtained by using the purely theoretical potential (solid curve in Fig. 1) strongly supports the validity of both our line broadening theory and the theoretical potential of Stevens and Robert.[5]

The HCl–Ar calculation, in conjunction with the previous calculations on CO_2–Ar and CO_2–He, provides a particularly strong confirmation of the line broadening theory and the theoretical potentials because these systems are so dissimilar. First, the rotational constant for HCl is 20 times greater than that for CO_2, making the elastic and inelastic collision processes quite different. Secondly, the center of mass for CO_2 lies at the center of the molecule while for HCl it is almost coincident with the Cl nucleus which means that the anisotropic forces and the torques exerted on the molecule are completely different. Thirdly, the symmetry of CO_2 causes all odd order anisotropies to vanish whereas in the case of HCl the odd terms (i.e., V_1, V_3, etc.) play an equally important role, particularly in the inelastic processes. Finally the vibrational effect which may have been present for CO_2–Ar seems to be absent, at least for the lower vibrational states in HCl–Ar (as evidenced by the agreement between the experimental results for the 0-0 and 0-1 vibrational bands shown in Fig. 1).

---

*Research performed while visiting professor at the Universite de Provence.

[1] E. W. Smith, M. Giraud, and J. Cooper, J. Chem. Phys. **65**, 1256 (1976).

[2] G. A. Parker, R. L. Snow, and R. T Pack, J. Chem. Phys. **64**, 1668 (1976).

[3] R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972).

[4] W. J. Stevens and D. Robert (manuscript in preparation for J. Chem. Phys).

[5] W. B. Neilsen and R. G. Gordon, J. Chem. Phys. 58, 4149 (1973).

[6] R. K. Preston and R. T Pack (to be published in J. Chem. Phys.)

[7] H. E. Scott (Ph.D. thesis, Ohio State University, 1973).

[8] J. Pourcin (Ph.D. thesis, Universite de Provence, Marseille, France, 1974).

[9] H. A. Gebbie and N. W. B. Stone, Proc. Phys. Soc. London **82**, 309 (1963).

[10] A. Levy, E. Piollet-Mariel, and C. Boulet, J. Quant. Spectros. Radia. Transfer. **13**, 673 (1973).

[11] J-P Houdeau, M. Larvor, and C. Haeusler, J. Quant. Spectros. Radia. Transfer. **16**, 457 (1976).

[12] H. Babrov, G. Ameer, and W. Benesch, J. Chem. Phys. **33**, 145 (1960).

[13] D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Mol. Spectrosc. **13**, 87 (1964).