Temperature dependence of rotational linewidths in HCl perturbed by argon

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In recent papers[1,2] we have developed a semiclassical theory for spectral line broadening in linear molecules perturbed by atoms. In that theory, the nuclei move on curved classical trajectories determined by the isotropic part $V_0(r)$ of the atom−molecule interaction potential. The perturbation of the molecular rotation vibration states due to a collision with an atom is described by an S matrix which is simply the exponential of a phase shift matrix η [see Eq. (2.6) of Ref. 1] which contains the anisotropic part $V'(r, \theta)$ of the atom−molecule interaction. The validity of this theory has been tested[1-3] by comparison with other semiclassical theories, purely classical theories, and purely quantum mechanical close coupling calculations. Its validity was confirmed in the sense that it agrees to within 10% with close coupling calculations (i.e., a numerical solution of the fully quantum mechanical Schrödinger equation for scattering).

Since this theory has no adjustable parameters (such as impact parameter cutoffs, etc.) it is ideal for testing the new theoretical potential surfaces based on the Gordon−Kim[4] electron gas model for repulsive forces. In Ref. 2, calculations were made for several rotational lines in HCl perturbed by Ar using the theoretical potential surface developed by Stevens and Robert[5] as well as the semiemperical potential of Neilsen and Gordon.[6] Even though these potential surfaces are completely different, it was found that both potentials produced very good agreement with experimental data for a wide range of rotational lines. It was thus concluded that line broadening data are not sufficiently sensitive to anisotropies in the potential surface to permit a determination of the interaction potential. However, this analysis was performed for a single temperature, 300 K, and it was felt that the temperature dependence of the half-widths might be more sensitive to anisotropies because high temperatures are determined more by the repulsive wall whereas low temperatures will be more strongly affected by the long range attractive forces. Unfortunately this was found to be an insignificant effect even over a temperature range from 125 to 1200 K. Nevertheless, the analysis of this temperature dependence proved to be quite interesting due to the apparent presence of a vibrational effect (i.e., an increase in linewidth caused by a distortion of the molecular potential curves for higher vibrational levels[7]).

In Figs. 1 and 2, recent measurements of the temperature dependence of the half-width[8-11] are compared with theoretical calculations for various rotational transitions

$(j+1 \leftarrow j)$ in HCl perturbed by Ar. The solid data points represent transitions in the fundamental vibrational band $(v, v' = 0, 1)$ and the open points represent pure rotational transitions $(v, v' = 0, 0)$. The theoretical calculations employed the semiclassical theory discussed above with the theoretical potential surface of Stevens and Robert[5]; cal-
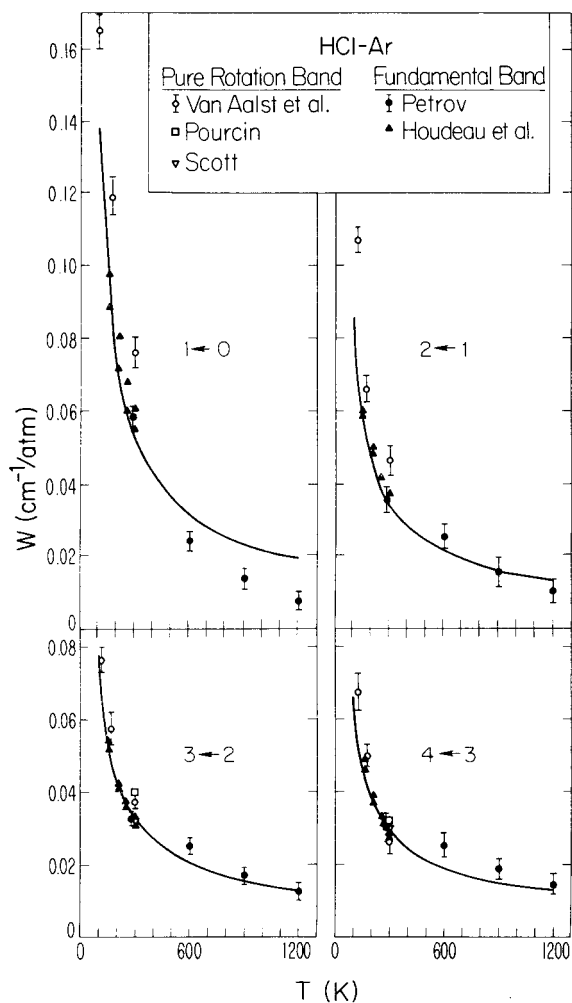

FIG. 1. Temperature dependence of halfwidths W for rotational transitions $j+1 \leftarrow j$ in HCl perturbed by argon. Solid points refer to measurements in the fundamental vibration band $(v, v' = 0, 1)$ and open points refer to pure rotation $(v', v = 0, 0)$; the curve represents theoretical calculations for the pure rotation band.

culations were also made with the semiemperical potential of Neilsen and Gordon[6] but they differed by at most 10% so they were not plotted. The present theoretical calculations do not take account of any vibrational effect because the only potential surface currently available is for the $v = 0$ vibrational level.

The agreement between theory and experiment is excellent for the lower rotational levels, $j \lesssim 6$ but the agreement becomes rather poor at low temperatures $T < 300$ K for the higher rotational levels $j > 7$. This could be due to systematic errors in the experimental procedure used by Miziolek, however, his data do converge to the measurements of Rank et al.,[12] Levy et al.,[13] and Babrov et al.[14] at 300 K (the results of Levy et al. and Babrov et al. were not plotted because they would obscure other data points). This disparity could also be due to theoretical errors, however, the theory agrees quite well with the 6–5 transition for low temperatures and one would expect a decrease in half width going to the 7–6 transition (the inelastic cross section decreases because the

energy level spacing increases with increasing j). In this regard, we note that the half-widths measured by Miziolek for the 7–6 transition in the fundamental band are larger than those measured by Van Aalst et al.[10] for the 6–5 transition in the pure rotation band whereas one would expect just the opposite. This may be an indication of vibrational effects at these low temperatures which should be checked by further measurements for the 0–0, 0–1, and 0–2 vibrational bands particularly for the higher rotational lines such as 7–6.

For higher temperatures, $T \gtrsim 600$ K, the calculations agree fairly well with the data of Petrov[9] except for the 1–0 transition where the theory is least accurate. Nevertheless, the experimental points do lie systematically above the theory for the higher lines. In fact, the data of Miziolek and Petrov for the 8–7 and 9–8 transitions give the distinct impression that the half-widths in the fundamental band are about 50% larger than the calculated values. We have therefore included the data of Pourcin[15] and Scott[16] for the pure rotational band measured at 300 K. Their data agree perfectly with the theoretical calculations again leading us to the conclusion that there is an effect due to vibration.

We thus conclude by noting that there is a need for more experimental data on the temperature dependence of the halfwidth for the higher rotational transitions (i.e., 7–6 and higher) in various vibrational bands, particularly in the pure rotational band where such data are almost nonexistent. If the presence of a vibrational effect is thus confirmed, there will also be a need for potential surfaces for the $v = 1$ and higher vibrational levels.
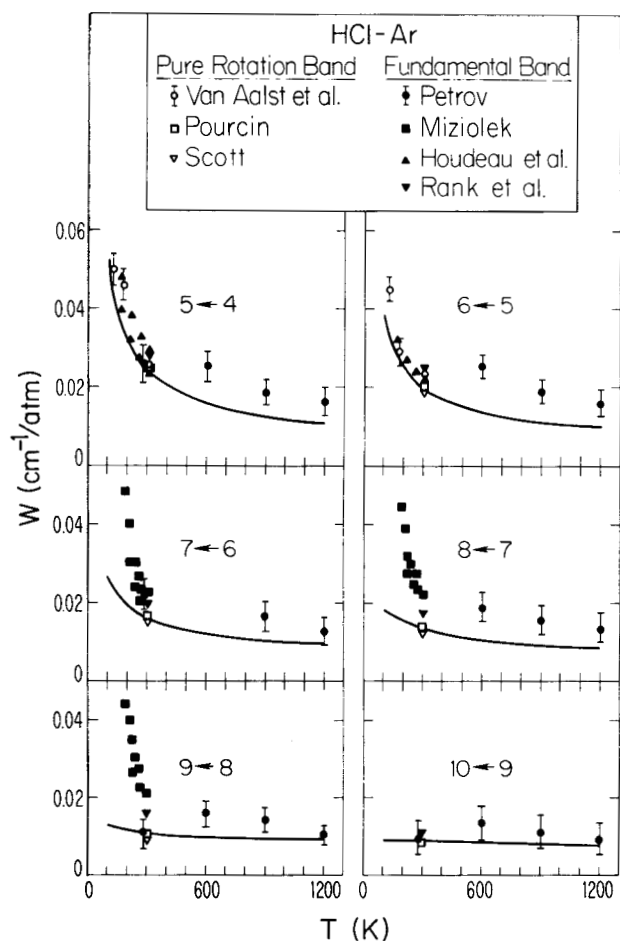

FIG. 2. Temperature dependence of halfwidths W for rotational transitions $j + 1 \leftarrow j$ in HCl perturbed by argon. Solid points refer to measurements in the fundamental vibration band (v, $v' = 0$, 1) and open points refer to pure rotation (v', $v = 0$, 0); the curve represents theoretical calculations for the pure rotation band.

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