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Comment on "Ortho-Para-Dependent Pressure Effects Observed in the Near Infrared Band of Acetylene by Dual-Comb Spectroscopy"

A recent Letter [1] reports oscillations between the pressure-broadening coefficients of C_2H_2 lines associated with *ortho* and *para* rotational levels. We show that they are due to the analysis of the spectra with an improper line shape [the Voigt profile (VP)] and that they practically vanish when a better-adapted profile [the Galatry profile (GP)] is used.

It is well known [2] that the VP inaccurately describes the shape of absorption transitions of molecular gases. Adjustments of observed lines with a VP provide underestimated (all the more so as the pressure is low) collisional widths Γ_C with maximal fit residuals when the collisional-to-Doppler widths ratio is around unity [3–5]. Consider a line, of absorption coefficient vs wave number $\alpha(\sigma)$, whose transmittance $\tau(\sigma) = \exp[-\alpha(\sigma)L]$ is recorded for a path length L. If the absorbance $A(\sigma) = \alpha(\sigma)L$ is fitted with the VP, the retrieved collisional width is obviously independent of L. It is the same if the transmittance is adjusted, as long as the exponential is in the linear regime [$A(\sigma) \ll 1 \Rightarrow \tau(\sigma) = 1 - A(\sigma)$]. On the other hand, L-dependent values are obtained in the nonlinear regime, due to the inaccuracy of the VP. This is the situation in [1] [Fig. 2(a)] where the intense even and odd J lines have significantly different peak absorptions, falling in the nonlinear regime of the transmittance and oscillating with J due to their (1:3) spin statistical weights. The approximations in the VP then lead to errors on Γ_C that are different for adjacent lines.

We have reanalyzed the $R(7)$ to $R(10)$ spectra at 2654 Pa [1] provided to us by Okubo. We first made fits using the VP for the absorption coefficient. This was applied to measured absorbances, transmittances (exactly as done in [1]), as well as transmittances in which the *ortho*:*para* weights were reversed from 3:1 to 1:3 [by changing $\tau(\sigma)$ around the $R(7)$ and $R(9)$ lines to $\tau(\sigma)^{1/3}$ and those around the $R(8)$ and $R(10)$ lines to $\tau(\sigma)^3$]. Fits were also made using the GP [6], which is much better adapted for the considered pressure. First, note that the VP fit residuals are large. For the $R(10)$ absorbance, they reach $\pm 1.5\%$ of the peak value and show the W shape typical of a line-narrowing effect [2–5]. This is expected since, for $P = 2654$ Pa, the collisional-to-Doppler widths ratio is about 0.5, within the range in which the Dicke narrowing process is the most efficient [2,3]. The GP fit residuals are reduced down to 0.5% of the peak, essentially within the noise.

The results are displayed in Table I. The values obtained with the VP strongly depend on the fitting choice and optical depth, with an inversion of the oscillations between columns 3 and 4. This confirms the inaccuracy of this profile and indicates that the even to odd J oscillations reported in [1] are due to the optical depth. In contrast, with the GP, all fits lead to consistent and, thus, much more reliable results, and the oscillations are considerably reduced. Finding out if the small ones remaining are true or due to noise requires fits of all lines at all pressures, a study that the authors of [1] may consider carrying out. Note that no oscillations were reported either in previous experimental or theoretical studies of C_2H_2 self-broadening (e.g., [7–11]).

Table I. Collisional widths (HWHM, in 10^{-3} cm^{-1}) obtained from VP and GP fits of measured absorbances (column 2), transmittances (column 3), and transmittances with switched *ortho*:*para* weights (column 4).

Line	Absorbances	Transmittances	Transmittances
		VP	
$R(7)$	3.69	4.21	3.88
$R(8)$	3.56	3.72	3.98
$R(9)$	3.66	4.14	3.83
$R(10)$	3.70	3.85	4.05
		GP	
$R(7)$	4.16	4.16	4.16
$R(8)$	3.96	3.93	3.94
$R(9)$	4.08	4.08	4.08
$R(10)$	4.07	4.03	4.02

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