COMMENT: REPLY TO COMMENT ON “DYNAMICS OF THE B $^3\Pi(0_u^+)$ AND A $^3\Pi(1_u)$ STATES OF CHLORINE BY LASER INDUCED FLUORESCENCE”

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(Received 22 September 1993)

The comment of Billy *et al.*¹ on our paper about the dynamics of the B and A states of chlorine² emphasizes mainly two points: a) our results about the radiative decay rate of the B state of Cl₂ are incorrect, because our experimental system is unable to measure the true long lifetimes of this state; b) both A $^3\Pi(1_u)$ and $^1\Pi(1_u)$ states contribute to the Coriolis predissociation in the B state, in contradiction with our mechanism, which excludes the $^1\Pi(1_u)$ state.

Concerning the first point, it is clear that the cylindrical cell used in our work has insufficient dimensions to make quantitative measurements of the long lifetimes expected in the B state of Cl₂. We are aware of that limitation, and this was clearly expressed in our paper², so we did not attempt to give quantitative values. However, the lifetime values measured for the $v = 5$ –12 vibrational manifold of the B state show important relative variations (100–200 μ s interval), considerably higher than the experimental error associated with every lifetime measurement. Although these will not be true lifetime values, their relative variations should be of physical significance. We cannot find any reason why simple geometrical cell limitations should affect the various vibrational levels in a different form. The only explanation we can find is that these variations reflect a real lifetime change with the vibrational level, though we did not make a quantitative evaluation of this phenomenon. We think that the best way to verify this point is to make lifetime measurements for these levels in a better suited experimental system.

Relative to the predissociation mechanism, Billy *et al.*¹ conclude that the potential energy curves of the A and B states of chlorine do not cross, and that both A $^3\Pi(1_u)$ and $^1\Pi(1_u)$ states contribute to the Coriolis predissociation, in contradiction with our

interpretation² and that of Heaven and Clyne³, which indicate that only the A state is responsible for the predissociation. In a previous work⁴, Billy *et al.* present the main conclusions of their analysis. They calculated predissociation constants k_v for different v vibrational levels of the B state. In figure 8 of their work, a plot of their calculated values is shown, in addition to the experimental ones obtained by Clyne and Martínez⁵. According to Billy *et al.*, the best fit to the experimental data is reached by considering that the ${}^1\Pi(1_u)$ repulsive state makes a significant contribution to the gyroscopic predissociation, besides the A ${}^3\Pi(1_u)$ bound state.

Several investigators^{6,7,8} have shown that the exact dependence of k_v with v is very sensitive to the shapes of the interacting potential energy curves. According to Mulliken⁹, when the potential energy curves cross in the attractive branch of the bound potential (external crossing, or "case +", predissociation), the vibrational dependence of k_v with v exhibits marked fluctuations: it is a well-established result¹⁰ that the k_v calculations for the B- ${}^1\Pi(1_u)$ systems present in the halogens I_2 and Br_2 show a very characteristic pattern, consisting in a very pronounced maximum for the vibrational level immediately above the crossing point with the B state, followed by a deep minimum, and finally one or several secondary maxima for higher v , depending on the concrete shape of the repulsive potential. On the other hand, when the potential energy curves cross in the repulsive branch of the bound potential (the case of B-A ${}^3\Pi(1_u)$ interaction), the k_v pattern shows a smooth decreasing trend with v . We made Franck-Condon density calculations for the B- ${}^1\Pi(1_u)$ system² to verify this point, using several trial functions for the repulsive potential, always obtaining marked oscillating patterns. We also considered mixed B-[A ${}^3\Pi(1_u)$ + ${}^1\Pi(1_u)$] contributions, but the introduction of any relevant component from the ${}^1\Pi(1_u)$ state always resulted in oscillations. This behavior appeared for any R_e value for the A state from $R_e = 2.43$ to 2.49 Å.

The oscillating structure is clearly visible in the calculations of Billy *et al.* for the B-[A ${}^3\Pi(1_u)$ + ${}^1\Pi(1_u)$] model: a high maximum in k_v for $v = 13$, followed by a minimum in $v = 18$, and finally a secondary maximum in $v = 20$. Clearly this behavior is due to the contribution of the ${}^1\Pi(1_u)$ state, which shapes the smooth contribution from the A state. A slight oscillating pattern in the k_v values measured by Clyne and Martínez can also be observed, though much less pronounced than for the calculations. Particularly, the slope $\Delta k_v/\Delta v$ for the lowest calculated vibrational levels ($v = 13$ – 17) is considerably higher than in the experimental values. We remeasured these k_v values², in qualitatively good agreement with the values of Clyne and Martínez, but were not able to detect any secondary maxima around $v = 20$, and the $\Delta k_v/\Delta v$ value for $v = 14$ – 17 is even lower than for the previous experimental values. Consequently, we think that there is no evidence of any significant oscillating behavior in the experimental data. This pattern is difficult to harmonize with a significant contribution from the ${}^1\Pi(1_u)$ state to the predissociation, which unavoidably produces the marked oscillatory pattern described above.

To conclude, in our opinion, no obvious oscillating pattern is present in the experimental data set of k_v values, and we think that a better fit to these data is obtained considering only the B ${}^3\Pi(0_u^+)$ -A ${}^3\Pi(1_u)$ interaction model. In the light of these results,

it is difficult to explain how the $^1\Pi(1_u)$ repulsive state can make a significant contribution to the gyroscopic predissociation mechanism.

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