COMMENT: “DYNAMICS OF THE $B^3\Pi(0_0^+)$ AND $A^3\Pi(1_u)$ STATES OF CHLORINE BY LASER INDUCED FLUORESCENCE”

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The paper by Martinez *et al.*¹ describes their study of the decay of the Cl_2 B state by radiative and predissociation processes. The results of this work and the conclusions of their analysis are in strong disagreement with our results.^{2,3} We want to clarify these uncertainties in the present comment.

1. THE RADIATIVE DECAY RATE OF THE B STATE OF Cl_2

The levels below the predissociation threshold ($v \leq 12$) surely must have a very long lifetime τ . Lifetimes of such a length are difficult to measure in a cell experiment because of molecular diffusion and quenching when the excited molecules reach the walls. This difficulty is illustrated by the previous literature values for the Cl_2 B state lifetime: $\tau = 83 \pm 5 \mu s$,⁴ $\tau = 305 \pm 15 \mu s$.⁵ These two different values were obtained by the same technique, in the same research group, simply by changing the cell geometry. Clearly, at very low pressures, the measured value for the lifetime is limited by the time of free flight to the walls. The cylindrical cell used in reference [1] has a radius of 6 cm, and the free flight to the wall takes typically 200 μs at normal temperature. This limitation is quite severe and explains why the lifetime measurements reported in [1] are all in the range 100–200 μs . On the contrary, our

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experiment^{2,3} used a novel technique⁶ which we think is better suited to the measurement of long lifetimes. A supersonic molecular beam is crossed at right angles by the beam from a single frequency laser, interrupted by an acousto-optic modulator to produce excitation pulses. The fluorescence detector is placed far downstream, facing the molecular beam. In this way, the photon collection efficiency is easier to model, since it depends upon the location of photon emission and thus the time of arrival of photons at the detector. This efficiency increases with time and has an interesting consequence: if the excited state has a sufficiently long lifetime, the increase in detection efficiency can more than compensate for the population decay, and the fluorescence signal will then increase with time. This gives a lower limit to the lifetime of the excited state. From the complete analysis of our results we have obtained a lifetime for the levels $v = 12$, $J = 0$ and 4 (which are simultaneously excited)

$$\tau = 1200 \pm 400 \mu\text{s}$$

This result is in good agreement with the value that can be deduced from the B–X transition dipole moment D_{BX} . A similar analysis was first done by Coxon,⁷ who used the unresolved absorption spectrum of Cl_2 to deduce the dipole moment. We have somewhat augmented this analysis by taking into account the r -dependence of D_{BX} and by calculating the radiative decay rate $\Gamma_{\text{rad}} = \tau^{-1}$ as a function of the vibrational level using the Julienne-Tellinghuisen approximation.⁸ An interesting result is that the decay rate $\Gamma_{\text{rad}}(v)$ behaves like $\omega_v = \partial E / \partial v$ when approaching the dissociation limit. This result can be demonstrated by simple arguments⁹ and in the present case it appears to be a good approximation as soon as $v \geq 15$.

Finally, a view is expressed in [1] concerning the A–B mixing. Since the A state is longer lived, this mixing will induce a lengthening of the B state radiative lifetime. However, the A–B coupling is a $\Delta\Omega = 1$ heterogeneous coupling, dominated by the Coriolis term. Accordingly, the resultant mixing should be noticeable only for large J levels and near local perturbations (which are well characterized¹⁴). In particular, our measurement of the radiative decay rate performed on the $v = 12$ $J = 0$ and 4 levels should not be affected by this effect.

2. HYPERFINE PREDISSOCIATION OF THE B STATE

In their paper, Martinez *et al.*¹ quote our measurement of the lifetimes of the level $J = 0$ in $v = 12$ and 13 (1200 and 50 μs respectively). They comment on this result by saying that “such large variations between adjacent vibrational levels are not expected to occur”. This idea has no foundation as the predissociation threshold is found to lie between these two levels, and the predissociation decay rate may be considerably larger than the radiative decay rate. Moreover, the vibrational dependence of the hyperfine predissociation³ is roughly similar to the vibrational dependence of the Coriolis predissociation.^{4,1} This suggests that the same electronic state is responsible for both predissociations, but we have shown that the story is evidently more complex.

3. THE A STATE POTENTIAL CURVE AND THE PREDISSOCIATION MECHANISM

Martinez *et al.*¹ calculate the Franck-Condon density for predissociation using various potential curves for the A state, assuming that it is the only $1u$ state responsible for the B state Coriolis predissociation. The agreement with the observed vibrational dependence of the predissociation rate is good only if the A and B state curves cross and if the equilibrium distance $r_e(A) = 2.48 \pm 0.01$ Å. A similar treatment was done several years ago by Heaven,¹⁰ with similar conclusions, but the conclusions about the position of the A state and its crossing with the B state are in contradiction with other evidences. Theoretical arguments due to Mulliken,¹¹ analogy with the other halogens,¹² and a recent spectroscopic study of the A state of Cl_2 ^{13,14} prove that the A and B state potential curves do not cross, and the data of references^{13,14} fix the equilibrium distance of the A state $r_e(A) = 2.4326$ Å. Moreover, we have shown in our paper³ that the assumption that the A and B states cross leads to an unrealistically large value of the Franck-Condon density and thus requires a very small value of the electronic matrix element in order to be in agreement with the observations. It would be very difficult to reconcile a small value of the electronic matrix element of the Coriolis coupling between the $\Omega = 0^+$ and 1 components of a $^3\Pi_u$ electronic state.

Finally, we have shown in our study that the two $1u$ states (A $^3\Pi_{1u}$ and $^1\Pi_{1u}$) both contribute to the Coriolis predissociation.

CONCLUSION

We think that the results of reference [1] concerning the radiative decay rate of the B state of Cl_2 are incorrect, because the technique used is not adapted to the very long lifetime of this state.

We also think that their analysis of the predissociation mechanism fails because it implies for the A state potential and the A–B Coriolis coupling values which cannot be reconciled with experimental and theoretical results. Furthermore, we think that the $^1\Pi_{1u}$ state also contributes to the Coriolis predissociation, and that the hyperfine predissociation is the dominant decay process for the levels $v \geq 13$, $J = 0$.

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