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COMMENTS

Comment on predissociation of O₂ in the *B* state

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In their paper on the predissociation of O_2 in the *B* state, Wodtke *et al.*[1] attempt to match the observed excitation spectrum of some O_2 Schumann–Runge features with simulated spectra synthesized from triplet component line center spacings, obtained from the fine structure analysis of Bergeman and Wofsy,[2] and individual triplet component widths, based on the calculations of Julienne[3] and Julienne and Krauss[4] for curve crossings of the $B\,^3\Sigma_u^-$ states of symmetries $^3\Pi_u$, $^5\Pi_u$, and $^3\Sigma_u^+$ (or $^1\Pi_u$), respectively. For example, the $R(27)$ feature of the (11,2) band, which is partially resolved in the experimental excitation spectrum of Fig. 4 of Wodtke *et al.*, is compared with three simulated spectra of which only one, viz., that corresponding to the curve crossing by the repulsive $^3\Pi_u$ state, is consistent, according to Wodtke *et al.*, with the experimental result. In their Fig. 4, the relative peak heights of the individual R_1, R_2, and R_3 components are given by the ratios of the reciprocals of the line widths of Julienne. These relative peak heights are used together with the component widths of Julienne and the component spacings calculated from the spin constants of

Bergeman and Wofsy[2] to generate three Lorentzians that are added to produce the resultant $R(27)$ line profile, which is then convoluted with the (assumed Gaussian) laser profile for comparison with the experimental excitation spectrum.

We have verified that the relative peak heights of the components, shown in Fig. 4 of Wodtke *et al.* on the same ordinate as the resultant cross section, are not the relative peak cross sections of the component Lorentzians, but are instead the relative integrated cross sections. This significant distinction, nowhere stated in their paper, confirms that the simulated spectra in their Fig. 4 are excitation spectra and not absorption spectra.

Wodtke *et al.* used the spin–spin and spin–rotation constants of the $v' = 11$ level of Bergeman and Wofsy[2] to calculate the triplet spacings for the $R(27)$ feature of the (11,2) band. Those spacings, estimated from Fig. 4 of Wodtke *et al.*, are $R_2 - R_1 \simeq 0.9$ and $R_3 - R_2 \simeq 1.2$ cm^{-1}. We have recently performed high resolution photographic absorption wavelength measurements of O_2 at ~ 520 K (unpublished), with the same spectrographic apparatus used in our earlier
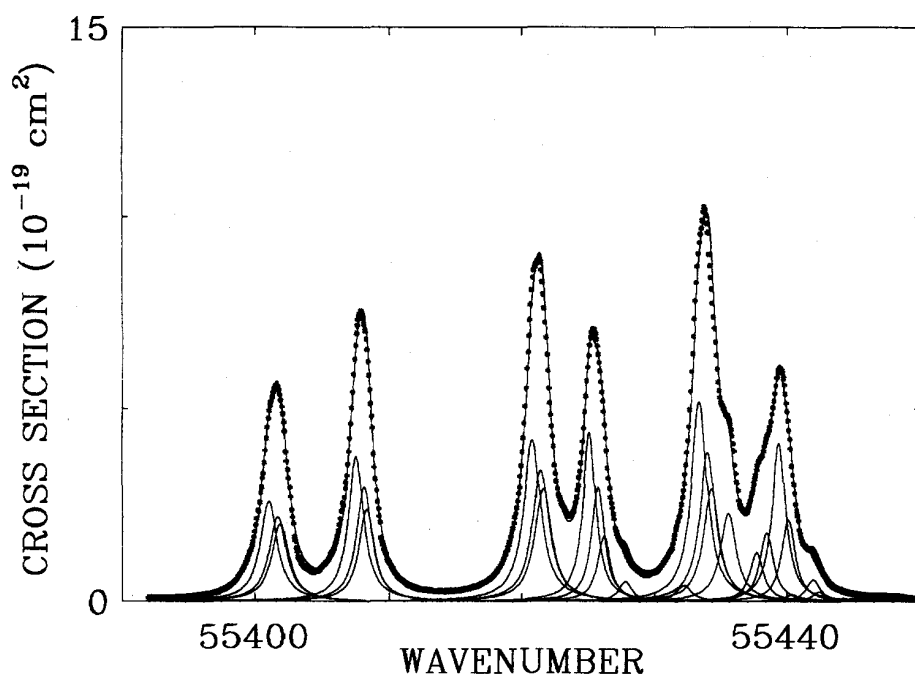
FIG. 1. Absorption cross section of part of the (11,0) Schumann–Runge band of O_2 at 79 K. Top curve, synthesized from lower fine structure component curves for a $^5\Pi_u$ predissociative mechanism, is fitted to measured cross sections (discrete points). Rotational assignments given in Fig. 2j of Yoshino et al. (1987) (Ref. 6).

work at lower temperatures[5]; the $R(27)$ triplet of the (11,2) band is resolved, and the measured spacings are $R_2 - R_1 = 1.7$ and $R_3 - R_2 = 1.0$ cm^{-1}. The significant difference between our experimental spacings and those used by Wodtke et al. would lead to significantly different resultant simulated line profiles.

We have no data on the absorption cross section of the $R(27)$ triplet of (11,2) band. However, we have measured the absorption cross section of the (11,0) band of O_2 at 79 K.[6] In Fig. 1, the discrete points show our measured values to which the uppermost curve has been fitted by an iterative

least squares procedure in which the fine structure components of any given line are represented by Lorentzians of equal width with line center positions calculated from our spectroscopic constants.[7] The component line widths (FWHM) producing this excellent fit are ~ 1.4 cm^{-1} (cf. ~ 1.2 cm^{-1} from absorption studies at lower resolution[8]), and the Lorentzian components are shown in the lower part of Fig. 1. The assumed ratio of component line widths (1:1:1) is very close to that predicted[3,4] for the $^5\Pi_u$ predissociative channel. In Fig. 2, the component line widths are in the ratios predicted[3,4] for the $^3\Pi_u$ predissociative channel,
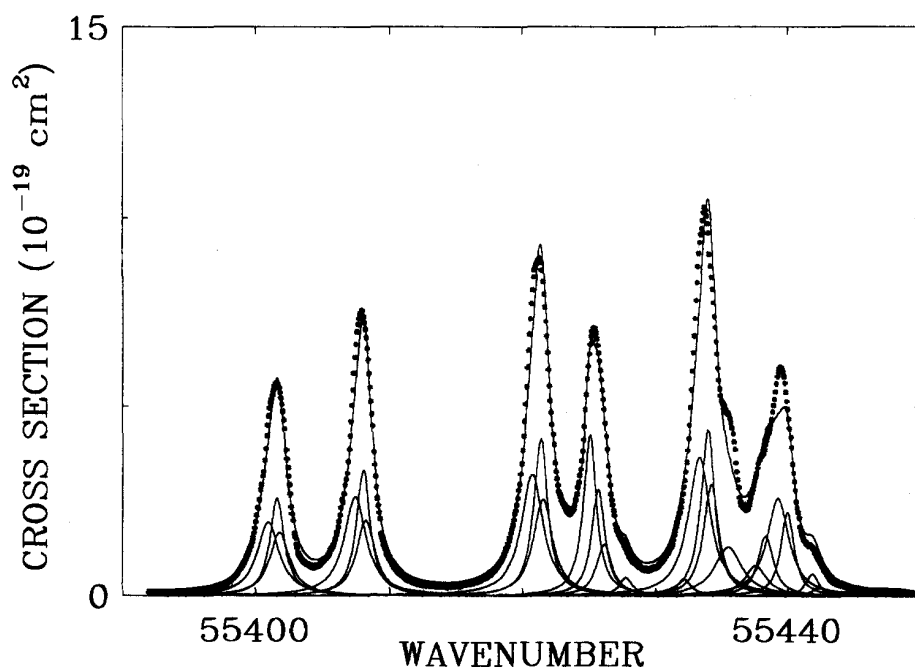

FIG. 2. Same as Fig. 1 except for a $^3\Pi_u$ predissociative mechanism.

which is the mechanism inferred as predominant by Wodtke *et al.* Near the band head region, where our measurements show the most detailed structure, the fitting is clearly superior in Fig. 1. The other, relatively structureless, features in Figs. 1 and 2 are fitted comparably well in both cases, and do not permit discrimination between $^5\Pi_u$ and $^3\Pi_u$ predissociative mechanisms.

Our results near the (11,0) band head, which are consistent with a $^5\Pi_u$ but not a $^3\Pi_u$ predissociative mechanism, do not necessarily apply to the $N = 27$ level, but suggest that the predominance of the $^3\Pi_u$ mechanism inferred by Wodtke *et al.* is not established, especially in view of the uncertainties in their simulated excitation spectra of $R(27)$.

In brief, we find the conclusions of Wodtke *et al.* concerning the predissociation of the $v' = 11$ level of the $B^3\Sigma_u^-$ state of O_2 to be unjustified. We have work in progress for the determination of the predissociation line widths of the (1,0)–(12,0) Schumann–Runge bands from our high-resolution results for the absorption cross sections[6] and spectroscopic constants for the B state.[7]

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Reply to: Comment on predissociation of O₂ in the *B* state

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In their comment on our paper[1] Freeman *et al.* question the interpretation of the line profile measurements of the *SR* $11\leftarrow2, R(27)$ triplet. We have consequently remeasured this and a number of other triplets ($v' = 10$ and $11, J' > 15$) with much higher signal to noise. The F_1:F_2:F_3 spacings are 1.7 and 1.2 cm^{-1}, respectively. This is in close agreement with calculations based on Freeman's molecular constants derived from new high resolution absorption data.

We are also able to derive the absolute spin-state dependent predissociation lifetimes, which have been shown to be very sensitive to the predissociation mechanism.[1,2] It is impossible to rationalize these data on the basis of spin–orbit coupling to a repulsive $^5\Pi_u$ surface. This is the mechanism that is used to explain the absorption spectra at 79 K, where only low rotational states are seen and the individual triplets are not resolved.

A real discrepancy between the experiments could be explained if significant predissociation via the orbit–rotation mechanism occurs, which would show a large rotational state dependence. We are analyzing our data in this context and the results, which may be able to unify the measurements of absorption and excitation spectroscopy, will be forthcoming.

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