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Resolution of the Discrepancy Concerning the A' Values of the NO_2 5933 Å Band

The recent analyses of the 5933 Å region of NO_2 by Stevens and Zare (*1*) and by Tanaka, Field, and Harris (*2*) yielded drastically different values of the excited-state rotational constant A', namely, 7.85 and 8.52 cm^{-1}, respectively. Using the method of laser-induced fluorescence Stevens and Zare (SZ) assigned transitions to various members of the $K_a' = 0, 1$, and 2 subbands. They found that the intensity of the K_a' subbands decreases with increasing K_a', indeed more rapidly than would be expected if the transition strengths followed the Boltzmann distribution. The value of A' was determined by SZ using

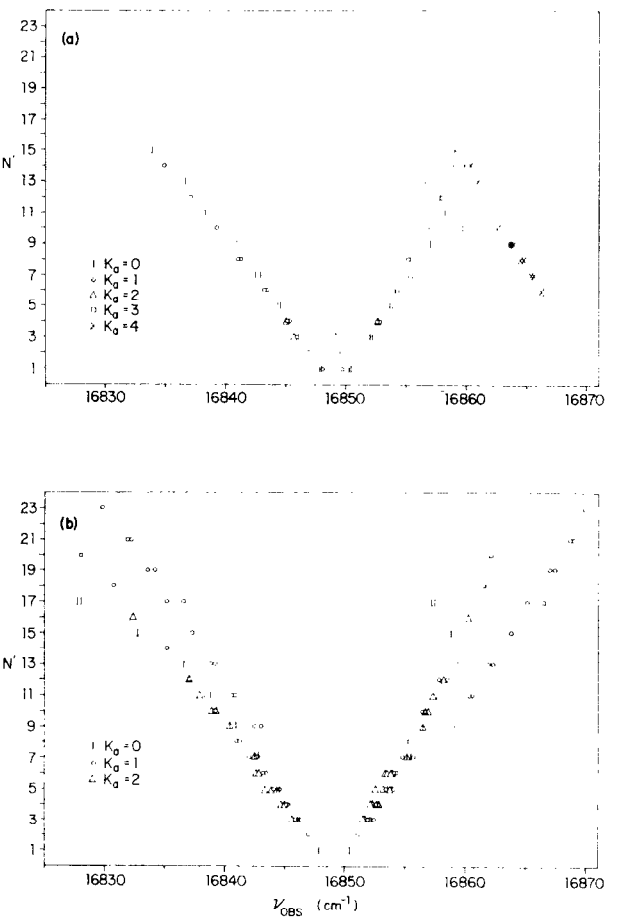

FIG. 1. Modified Fortrat diagram of the 5933 Å region as analyzed by (a) Tanaka, Field, and Harris (*2*) and by (b) Stevens and Zare (*1*).

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an iterative least-squares asymmetric top computer program. It should be noted that SZ also observed some members of a $K_a' = 3$ stack. The intensity of these members seemed comparable to the $K_a' = 0$ stack, but these were not included in their analysis because they "appear to be caused by a band whose origin lies further to the blue."

Tanaka, Field, and Harris (TFH) also employed laser-induced fluorescence as well as optical–microwave double resonance to observe transitions to members of the $K_a' = 0$, 1, and 2 subbands, and the P branch of $K_a' = 3$ and 4 subbands. Once again the intensity decreased with increasing K_a' for the first three subbands. However, TFH report that the intensity of the $K_a' = 3$ subband is comparable to $K_a' = 2$, and that of $K_a' = 4$ to that of $K_a' = 1$. The subband origin and $\bar{B}'$ value were found for each subband by a simple least squares program. Although they noted an "appreciable discontinuity" between the $K_a' = 2$ and $K_a' = 3$ subband origins, TFH proceeded in their analysis to assume that all the K_a' subbands belong to the same vibronic band. When TFH combine the data for all the subbands, the resulting value of A' is much larger than that derived by SZ.

Figure 1a presents a modified Fortrat diagram for the transition reported by TFH. Here the values of N' for each K_a' stack are plotted against the observed line positions. It is seen from this figure that the $K_a' = 3$ and 4 subbands appear to have an altogether different vibronic origin than $K_a' = 0$, 1, and 2. The possibility exists that some K-dependent perturbation is causing this behavior. However, the intensity variation with K_a' seems to argue against this interpretation, since the intensity would be expected to either increase or decrease smoothly with K_a'. Alternatively, the $K_a' = 3$ and $K_a' = 4$ subbands may not belong to the 5933 Å band (16 849.48 cm^{-1}). From the subband origins for $K_a' = 3$ and $K_a' = 4$, an A' value of roughly 7.95 cm^{-1} is obtained. This A' value, in conjunction with their $\bar{B}'$ value, places the vibrational origin at approximately 16 864 cm^{-1}. Using supersonic expansion cooling, Smalley, Wharton, and Levy (*3*) observe vibronic band origins at 16 849.8 (very strong), 16 868.6 (weak), and 16 875.5 cm^{-1} (strong). We suggest that the $K_a' = 3$ and $K_a' = 4$ subbands observed by TFH belong to one of the latter two bands. This reassignment removes the discrepancy in the reported A' values. However, the inertial defect problem still remains, suggesting that both bands are perturbed.

Figure 1b presents the corresponding modified Fortrat diagram for the transitions reported by SZ. All assignments are consistent with one vibronic origin, namely, 16 849.48 cm^{-1}. During the course of this investigation, a copy error was discovered involving $N'_{K_{-1}K_{+1}} = 17_{1,16}$ in Table I of SZ. The P-branch transitions $17_{1,16} \leftarrow 18_{1,17}$ should read 16 836.56 and 16 835.14 cm^{-1} for the two spin components, while the R-branch transitions $17_{1,16} \leftarrow 16_{1,15}$ should read 16 866.41 cm^{-1} and 16 865.09 cm^{-1}.

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David L. Monts and Richard N. Zare

Department of Chemistry
Columbia University
New York, New York 10027

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