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The Absence of Optical Pumping in Matrix-Isolated Magnesium

In a recent paper in this journal (1), the absorption spectra of matrix-isolated Mg_2 molecules was presented. Brewer and Wang reported the presence of two absorption peaks in the 3540-3700 Å region: a singlet at 3544 Å and a singlet near 3580 Å that split into a doublet at 3575 Å and 3590 Å upon warming of the matrix. They proposed that optical pumping of the

Fig. 1. Proposed pumping scheme to account for spectral features seen between 3540-3700 Å in matrix-isolated magnesium.

$1P^* \leftarrow 1S$ transition in undimerized Mg atoms, followed by radiationless decay to the $3P$ state would allow the $3D \leftarrow 3P$ transition to be observed. See Fig. 1. In this manner, they account for the absorption peaks at 3575 Å and 3590 Å.

This explanation raises several questions. Moore's tables (2) show that the energy difference between the $3P_1$ and $3D$ states in the gas phase amounts to 26087 cm^{-1} , indicating a matrix blue shift of 1768 cm^{-1} . A shift of this magnitude for Mg atoms in a krypton matrix has not been reported (3, 4); however, two excited states of the atom are involved in the $D^3 \leftarrow P^3$ transition and these could conceivably interact to a greater or lesser extent with the matrix than the previously examined $1P$ and $1S$ states. It appears that the $3D \leftarrow 3P$ transition could be responsible for either of the singlets reported by Brewer and Wang.

As mentioned by the authors, modulation of the exciting light should have a direct effect on the intensity of the triplet-triplet transition. In an attempt to verify the proposed pumping scheme, an experiment was performed in which light necessary for the $1P \leftarrow 1S$ transition was prevented from falling on the matrix target. The apparatus and experimental conditions were the same as those described in (1). The matrix and metal were codeposited, and the

FIG. 2. Microphotometer tracings of spectral features seen in matrix-isolated magnesium: (A) without filter, (B) with Kodak Wratten filter no. 35.

ultraviolet spectra recorded photographically. A tracing of the plate confirmed the spectra reported in (1). A second spectra was recorded, this time with a Kodak Wratten filter no. 35 placed between the xenon light source and the cryotip window. This filter effectively blocked the 2800–2850 Å light necessary for the singlet–singlet transition, but allowed the passage of 3000 Å to 4000 Å light. Tracings of the two plates are shown in Fig. 2. It can be seen that even after insertion of the filter, the spectral features in the 3540–3700 Å region persist. It is thus likely that the features are not the result of optical pumping in Mg atoms, but rather due to some as yet unidentified transition in Mg_2 molecules.

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