Detection by Magnetic Circular Dichroism of a Long-lived Excited State of Matrix-isolated Palladium Atoms

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Photolysis of matrix-isolated Pd atoms generates a transient species showing a very strong m.c.d. signal but no detectable absorption spectrum; the life-time of the species and the fact that it can be regenerated many times without significantly changing the absorption and m.c.d. spectra of the matrix, suggest that the transient is a long-lived excited state of Pd, rather than a photo-chemically generated aggregate or complex.

The electronic spectra of matrix-isolated Pd atoms were first reported by Mann and Broida.[1] The spectra were reinvestigated by Klotzbücher and Ozin[2] who showed that the long-wavelength bands seen earlier were due to Pd/N_2 complexes and that the true spectra consisted of a group of intense bands all lying below 260 nm. They assigned these bands to transitions from the $^1S_0$ ($4d^{10}$) ground state to states ($^1P_1$, $^3D_1$, $^3F_2$, and $^3P_1$) arising from the $4d^9 5p$ configuration.[3]

We have recently measured the absorption and m.c.d. spectra of Pd atoms in Ar and Kr matrices. The absorption spectra are unexceptional, but in the case of the m.c.d. experiment a remarkable photolysis reaction can be observed. This process, which is quite undetectable in absorption spectra, is the subject of this communication.

Palladium/noble gas matrices were prepared by conventional methods in our m.c.d./m.i. apparatus.[4] All experiments described were carried out at *ca.* 5 K. The absorption spectra agree well with those reported in the literature.[2] When scanned from longer wavelengths towards shorter, no m.c.d. signal can be detected above 250 nm, below which the m.c.d. spectrum of a diamagnetic species (temperature-independent spectrum) which corresponds well to the absorption spectrum is found, Figure 1. But, if the dichrograph is then returned rapidly to long wavelengths (*ca.* 375 nm) and the m.c.d. spectrum is remeasured, a new, exceptionally strong, and rapidly decaying m.c.d. signal is readily observable in the 290—360 nm region. This process, generation of the transient species by photolysis followed by measurement of its m.c.d. spectrum, can be repeated *ad lib.* with only slight changes in the quality of the matrix and the atomic spectra between 200 and 250 nm. Further, although the photolysis process must remove some of the atoms which are responsible for the 200—250 nm absorption and m.c.d., no diminution in these spectra could be detected. The transient species can also be generated by exposure of the matrix to other sources of radiation in the 200–250 nm region.
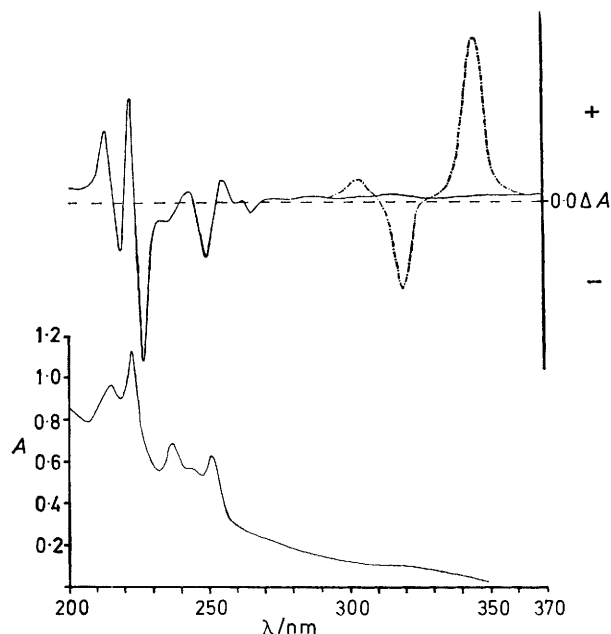

Figure 1. The absorption and m.c.d. spectra of palladium atoms in krypton. The broken line is the m.c.d. spectrum of the transient species. Full line = before photolysis.

Though the species responsible for it decays rapidly ($t_{\frac{1}{2}}$ of the order of seconds), the m.c.d. signal is extremely intense and can be recorded easily. All attempts to find an absorption band in the region have failed showing in this, as in other favourable cases,[5] the extreme sensitivity of the m.c.d. as compared to the absorption measurement.

The reproducibility of the experiment, the limited change in the atomic bands after many repetitions, the observation
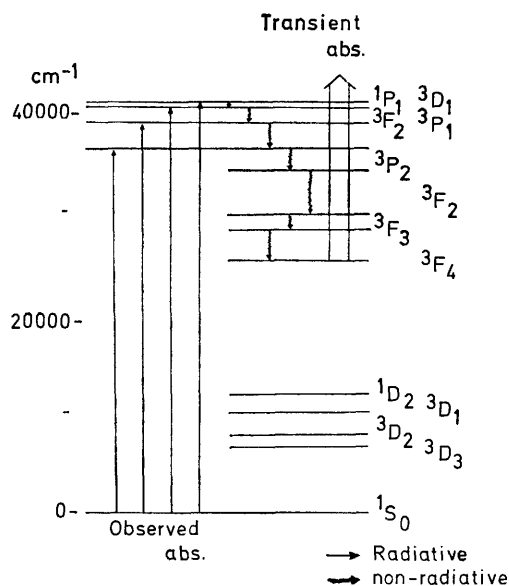
Figure 2. An energy-level scheme for gaseous palladium atoms (ref. 3) indicating the proposed ground state of the transient m.c.d. spectrum.

of the effect in both Ar and Kr matrices combined with the rapid decay, all suggest that the new species is a long-lived excited state of Pd rather than a new 'chemical' species such as Pd_2 or a Pd/noble gas complex. The remarkable strength of the m.c.d. signal as compared to the undetectable absorption, or the m.c.d. of the unphotolysed atoms, indicates that the transient species is paramagnetic.

In our view, the most likely ground state for the transient m.c.d. is $^3F_4$ ($4d^85s^2$) to which excited atoms could decay non-radiatively as indicated in Figure 2. One might expect a long life-time for a $^3F_4$ atom since further decay to the $^1D_2$ state requires a large energy loss ($ca.$ 13 000 cm^{-1}) which may be difficult to achieve non-radiatively, while radiative decay to the ground state is unfavourable on account of the high J number and the fact that it requires a parity-forbidden two-electron transition ($4d^85s^2 \rightarrow 4d^{10}$). The $^3D_3$ state, found at

6564 cm^{-1} in the gas phase,[3] could be reached from the $^3F_4$ by radiative energy loss and could, in principle, be the excited state which we have observed. However, we favour the $^3F_4$ on the grounds that it would be rather easier for the $^3D_3$ to lose its $ca.$ 7000 cm^{-1} non-radiatively than for the $^3F_4$ to lose $ca.$ 13 000 cm^{-1}, and we are looking for a state with a long life-time.

If the transient species is indeed a $^3F_4$ atom then the energy of that state ($ca.$ 25 000 cm^{-1} in the gas phase[3]) and the energy of the observed m.c.d. (29 000—33 000 cm^{-1}) suggest that the upper state(s) of the transient m.c.d. would be found between 54 000 and 58 000 cm^{-1} in the gas phase. (No matrix shift is included in the calculation since it is assumed that the major part of such a shift arises from the increased size of the excited state as compared to the ground-state atom. In this case both lower and upper states are excited states so their contributions to the shift should approximately cancel.) The above energy range embraces a large number of bands assigned to the $4d^85s5p$ configuration of Pd, most of which have not been fully assigned.[3] The experimental J values indicate that transitions from $^3F_4$ to a number of these states should be allowed.

Clearly, it is essential to the substantiation of the tentative interpretation above that the proposed long-lived excited state species be further investigated and its parameters, particularly its life-time, measured. We do not have the facilities for experiments of this type and we therefore publish our observations in the hope that others will feel that they are worth further study.

References

1 D. M. Mann and H. P. Broida, *J. Chem. Phys.*, 1971, **55**, 84.
2 W. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, 1976, **15**, 292.
3 C. E. Moore, 'Atomic Energy Levels,' U.S. Nat. Bur. Stand.' Washington, D.C., 1958.
4 T. J. Barton, R. Grinter, and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1978, 608.
5 I. N. Douglas, R. Grinter, and A. J. Thomson, *Chem. Phys. Lett.*, 1974, **28**, 192.