The Emission Spectrum of $HgAr^+$

By N. J. BRIDGE

(*University Chemical Laboratory, The University, Canterbury, Kent*)

Summary Emission from the ion $HgAr^+$ has been observed in low-pressure discharges: the high-resolution spectrum yields a full assignment of the transition and the length, vibrational frequency, and dissociation energy of the bond.

THE emission spectra of discharge tubes containing mercury vapour (10^{-3} torr) and argon (10 torr) show a short band system centred at 282 nm which does not appear in the spectra of either of the pure components. The bands were first observed with a commercial "bacteriocidal" lamp (internal electrodes, operating at 50 Hz a.c.) and later studied with a discharge tube filled in the laboratory and using radio-frequency excitation through external electrodes

	B (cm^{-1})	r (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})
Upper state	0·100	2·25	105	1·35	*ca.* 2000
Lower state	0·104	2·21	100	1·50	*ca.* 1700

The electronic origin, $\nu_e = 35{,}444$ cm^{-1}.

Under high resolution extended fine structure is visible. The vibrational analysis is straightforward and yields frequencies ω_e, anharmonicities $\omega_e x_e$ and estimated dissociation energies $D_e \simeq \omega_e^2/4\omega_e x_e$. The bands are degraded to the red and comprise three branches (P,Q,R). The P-branch of the 1–0 band is well-resolved over a wide range (30th—120th rotational levels) and gives a good value ($\pm$ 1%) for the difference between the rotational constants for upper and lower states, $B' - B''$. The sum $B' + B''$ is estimated ($\pm$ 5%) from the frequency interval between the R head and the origin. Hence one obtains the rotational constants and bond lengths r ($\pm$ 3%).

These data are interpreted by describing the emitting species as Hg^+ bound to Ar by a charge-induced dipole interaction. The electronic transition corresponds to the transition of the free ion Hg^+ between its ground state $5d^{10}6s(^2S_{\frac{1}{2}})$ and its first (metastable) excited state, $5d^9 6s^2$-$(^2D_{\frac{5}{2}})$, at 35514 cm^{-1}.

For a weak, van der Waals bond the electronic coupling in the molecule is expected to follow Hund's case (c); the total angular momentum of the mercury atom J_a couples to give a component Ω parallel to the internuclear axis. For the ground state of $HgAr^+$, $\Omega = J_a = \frac{1}{2}$; since the emission bands have Q branches, $\Delta\Omega = 1$. Thus the transition is forbidden in the free ion ($\Delta J = 2$) but allowed in the molecule.

The free ion transition is in fact observed (with an integrated intensity 300 times less than that of the band) and shows a large isotope splitting. This same pattern is repeated in the R heads of the molecular bands and is evident in the P branch of the 1–0 band. The effect is independent of the rotational state of the molecule and must be due to the splitting of the electronic origin.

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