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Experimental study of the cold mercury dimer

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The experimental setup has been previously described.[2] The cold mercury dimer is obtained in a continuous supersonic expansion of mercury in argon, through a $D = 200\,\mu$m nozzle ($P_0 = 3$ atm). The dimer concentration increases by two orders of magnitude when Ar is used as carrier gas instead of He (in the same conditions of temperature and pressure). The mercury is kept under an oven maintained at 300 °C (mercury vapor pressure of $\simeq 200$ Torr). The two laser beams (excitation and probe) cross the jet at $x/D = 30$, and are delayed by $\simeq 15$ ns. The free $\mathrm{Hg}(^3P_0)$ is monitored by the laser induced fluorescence of the $\mathrm{Hg}(^3P_0 \rightarrow 7^3S_1)$ transition.

Hg_2 has been a challenge for potential calculations.[3] The lowest predicted states are:

The ground state of the mercury dimer, correlated with $\mathrm{Hg}(^1S_0) + \mathrm{Hg}(^1S_0)$, is a 0_g^+ state.

The lowest u excited state 0_u^- correlates with the $\mathrm{Hg}(^3P_0) + \mathrm{Hg}(^1S_0)$ configuration and cannot be excited optically.

Two states with u symmetry (1_u and 0_u^+ correlating to $\mathrm{Hg}(^3P_1) + \mathrm{Hg}(^1S_0)$ can be excited: the 1_u state studied here is strongly bound while the 0_u^+ state is very weakly bound.

The fluorescence excitation spectrum of the cold mercury dimer in the 270–260 nm spectral region is presented in Fig. 1. It shows a long vibrational progression in the 1_u state. Each vibrational band has a substructure, 11 lines separated by about 5 cm^{-1} [Fig. 2(a)]. This structure can be assigned to an isotopic effect as for Hg–Xe complexes.[2,4] In natural mercury, six isotopes [$M_i = 198, 199, 200, 201, 202, 204$] are present in great abundance, the 21 possible combinations of the i, j isotopes lead to only 12 combinations of different ($M_i + M_j$) masses and all the lines can be assigned to different isotopic combinations as shown in Fig. 2(b) (the 204–204 combination, very weak, is not observed). From the strong isotopic shift and the linear Birge–Sponer plot, it was possible to deduce the vibrational quantum number v' of the excited vibrational bands, the vibrational frequency $\omega_e' = 133 \pm 1$ cm^{-1}, and the anharmonicity $\omega_e x_e' = 0.52 \pm 0.02$ cm^{-1} of the 1_u state, by using the well-known formula[5]

$$\Delta\nu_{12} = \mathrm{v}'(1 - \rho_{12})\Delta G_{v'+1/2} \quad \text{with} \quad \rho_{12} = (\mu_1/\mu_2)^{1/2},$$

μ_1, μ_2 being the reduced masses of two isotopic Hg_2 molecules and $\Delta G_{v'+1/2}$ the frequency separation of the successive v' and $v' + 1$ vibrational bands.

Hence in the Morse potential approximation, we can

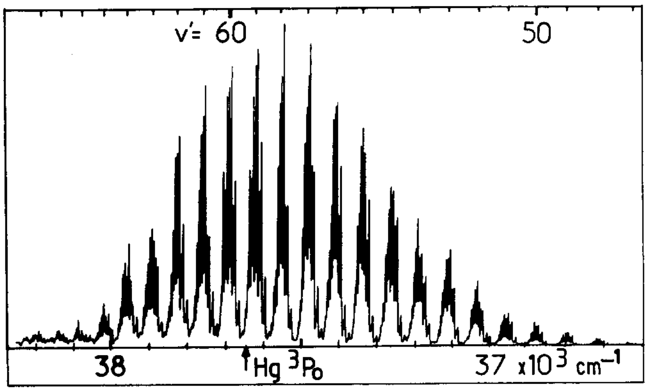

FIG. 1. Fluorescence excitation spectrum of the cold Hg_2, the arrow indicates the energy of the free $\mathrm{Hg}(^3P_0)$ $P_0(\mathrm{Ar}) = 3$ atm, $T_{\mathrm{Hg}} = 300$ °C, $D = 200\,\mu$m, $x/D = 30$.

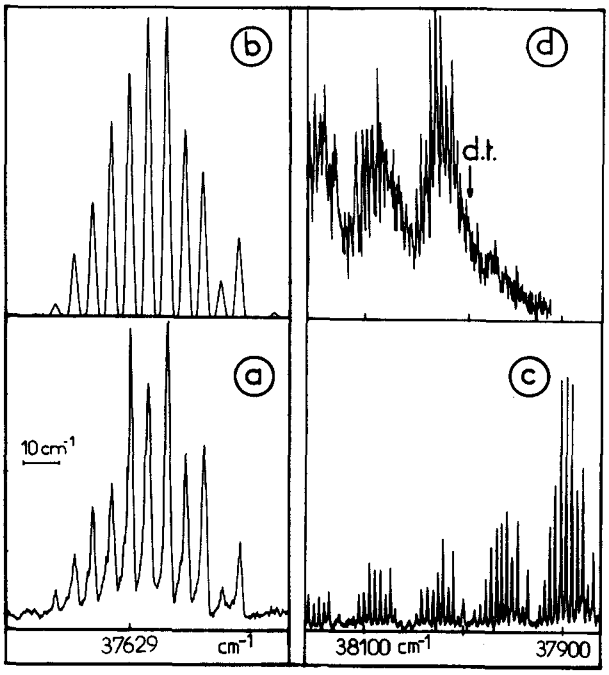

FIG. 2. (a) Expended view of the $v' = 60 \pm 1$ vibrational band. (b) Simulation of the isotopic substructure. (c) Expended view of Fig. 1, $v' = 63$, 64, 65, 66 ± 1. (d) Action spectrum: Excitation of the Hg_2 1_u state probe of the $Hg(^3P_0)$ free mercury through laser induced fluorescence. Below the dissociation limit of the 0_u^- state, no signal appears. Above the dissociation limit, $Hg(^3P_0)$ is obtained through the collision-induced relaxation. $1_u \rightarrow 0_u^- \rightarrow Hg(^3P_0) + Hg(^1S_0)$. (d.t.: dissociation threshold.)

deduce the well depth of this state $D_e(1_u) = 8450 \pm 200\ \mathrm{cm}^{-1}$.

We could get a precise value of the ground state binding energy, studying the collision induced electron relaxation of $Hg_2(1_u)$ in the jet provided by the mechansim:

$$Hg_2(x\,0_g^+) + h\nu$$
$$\rightarrow Hg_2(1_u, v') + \text{collision}$$
$$\rightarrow Hg_2(0_u^-,\ \text{dissociative}) \rightarrow Hg(^3P_0) + Hg(^1S_0).$$

This process was observed to be collision induced. Moreover, it has been shown[3] that no matrix elements directly couple the 1_u and the 0_u^- states in Hg_2. However, collisions will induce the relaxation by destroying the $C_{\infty v}$ symmetry of the molecule.

This process was not observed in the Hg–Ar[6] complex owing to a bad overlap of the bound and continuum wave functions, while the excitation of $v' = 60$ in the Hg_2 case increases the overlap by orders of magnitude.

The resulting free mercury in the $^3P_0$ state detected by laser-induced fluorescence will be observed only if the energy of the excited $(1_u,\ v')$ state exceeds the dissociation limit of 0_u^- to $^3P_0$. Using this threshold effect we can deduce the ground state 0_g^+ binding from the energy difference between the cutoff frequency of the $Hg(^3P_0)$ signal $[37\,990 \pm 20\ \mathrm{cm}^{-1}$, Fig. 2(d)] and the energy of the $Hg(^3P_0)$ free mercury ($37\,645\ \mathrm{cm}^{-1}$). We assumed a cold jet, i.e., the translational average energy being less than $5\ \mathrm{cm}^{-1}$, hence we find $D_0\ (X\,0_g^+) = 345 \pm 20\ \mathrm{cm}^{-1}$. This measurement implies that the 0_u^- potential has no barrier at long distance, in agreement with theoretical works.[3] From this measurement we can deduce the binding energy of the 1_u excited state to be $8260 \pm 200\ \mathrm{cm}^{-1}$.

Finally, assuming two Morse potentials, we can deduce the spectroscopic parameters for the $A\ 1_u$ and $X\,0_g^+$ states, as well as the difference in equilibrium distance between these two states ($R_e' - R_e'' = 1.1 \pm 0.1$ Å. In view of this result, the value $R_e'' = 3.3$ Å admitted in the literature[1,3] seems much too small.)

$X\,0_g^+$ $D_e = 350 \pm 20\ \mathrm{cm}^{-1}$ $\omega_e'' = 19 \pm 2\ \mathrm{cm}^{-1}$[7]
$\omega_e x_e'' = 0.25\ \mathrm{cm}^{-1}$,

$A\ 1_u$ $D_e = 8260 \pm 200\ \mathrm{cm}^{-1}$ $\omega_e' = 133 \pm 1\ \mathrm{cm}^{-1}$
$\omega_e x_e' = 0.52\ \mathrm{cm}^{-1}$.

These are preliminary results on the mercury dimer: a full analysis of higher excited states is in progress.

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