Far-Wing Excitation Spectra of the Hg6s6p$^3P_0$ – 6s7s$^3S_1$ Inter-Excited-State Transitions Broadened by Ar and Ne

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We have measured the laser-excitation spectra of the Hg–Ar and Hg–Ne collisional quasimolecules in the far wings of the Hg 6s6p $^3P_0$ – 6s7s $^3S_1$ inter-excited-state transitions broadened by Ar and Ne. The simulation of the spectrum, based on an uniform-semiclassical treatment for the free-free Franck-Condon factor, has been carried out for the Hg–Ar system in order to estimate the potential curves for the $E\ ^31$ and $a\ ^30^-$ states of the quasimolecule.

As is now well understood, the far-wing spectrum of a pressure-broadened atomic line is attributable to the optical transitions of quasimolecules formed transiently during a binary collision. Important information, therefore, can be drawn from the spectral line-shape in the far wings on the potential energy curves of the quasimolecule as well as the collision dynamics. Since the Cs - rare-gas (RG) interaction-potentials have been obtained succesfully from the far-wing spectra by Hedges, Drummond, and Gallagher in 1972,[1] a considerable number of studies have been devoted to the far-wing spectra of metal-atomic lines.[2] Most of them, however, are concerned with the resonance transitions to or from the ground state. No measurements has been made on a transition between the excited states both of which are optically inaccessible from the ground state. Here we report the first measurements of the far-wing spectra associated with the transitions between the 6s6p $^3P_0$ and 6s7s $^3S_1$ excited states of Hg broadened by RG's (Ar and Ne) ; the optical transitions are strongly forbidden between the ground $^1S_0$ state and both of those excited states.

Duval *et al.*[3] and Fuke *et al.*[4] have performed the laser-excitation study of the Hg–Ar van der Waals (vdW) molecule to obtain information about the potential-energy curves $V_E(R)$ and $V_a(R)$ for the $E\ ^31$ and $a\ ^30^-$ states correlated asymptotically to the dissociation limits of Hg*(7 $^3S_1$)+Ar and Hg*(6 $^3P_0$)+Ar, respectively. Most part of $V_E(R)$ has been determined with satisfactory accuracy by Duval *et al.* from the bound-bound laser-excitation spectra of the $E - A$ and $E - B$ transitions. However, $V_a(R)$, also given by the same group, may be much less accurate than $V_E(R)$ since it has been estimated from the $E \rightarrow a$ emission spectra measured with the spectral resolution of 10 cm^{-1}, where the vibrational progression has not been resolved. Moreover, their value for the dissociation energy of $V_a(R)$ is higher by 13 cm^{-1} than the one deduced by Fuke *et al.* from the bound-bound laser-excitation spectra of the $E - a$ transition . We will simulate, therefore, the far-wing spectrum of the 6 $^3P_0$ – 7 $^3S_1$ transition on the basis of a uniform semiclassical treatment for the free-free Franck-Condon factor.[5] The potential curves given by Duval *et al.* will be used at the start of simulation and then $V_a(R)$ will be modified to have a better agreement between the observed and calculated spectra.

Details of the experimental setup have been described elsewhere,[6] and only a brief discription is given here. The experiments were performed in a photon-beam-gas-cell arrangement. The Hg vapor was generated in a heat-pipe cell.

Table 1. Potential parameters for the E^31 and a^30^- states

	$^3P_0(a)$	$^3S_1(E_1)$	$^3S_1(E_2)$
ω_e (cm^{-1})	14.5	109	3.49
$\omega_e x_e$ (cm^{-1})	0.54	1.90	0.08
R_e (Å)	4.20	2.81	6.95
D_e (cm^{-1})	97	1430	38
β_2/β_1	2.00	2.10	1.01

CO (Nippon Sanso, purity > 99.95%) and one of the RG's : Ar (Nippon Sanso, purity > 99.9999%) and Ne (Nippon Sanso, purity > 99.996%) were admitted into the cell to give a total pressure of 510 Torr at 24°C ; the partial pressures were 500 Torr for RG and 10 Torr for CO. They were used without further purification. The third harmonic of a pulsed Nd:YAG laser (Lumonics YM-1000) was used to pump two dye lasers (Lumonics HD-500) simultaneously. One of their outputs was frequency doubled to generate the preparation pulse at 253.7nm by which the ground Hg(6 $^1S_0$) atoms were excited to Hg*(6 $^3P_1$). Hg*(6 $^3P_1$) was then quenched efficiently by CO every five collisions to give Hg*(6 $^3P_0$) through the intramultiplet transitions.[6] The other dye-laser output was scanned from 400 to 410 nm. It served as an excitation pulse in the measurements of the fluorescence-excitation spectra of the Hg*(6 $^3P_0$)-RG collisional quasimolecule in the far wings of the 6 $^3P_0$ – 7 $^3S_1$ line at 404.7nm brodened by RG. The pulse duration and the linewidth were about 6 ns and 0.05 cm^{-1}, respectively, for both the preparation and excitation pulses, and the pulse energies were typically 600 μJ for the preparation pulse and 1 mJ for the excitation pulse. The preparation and excitation pulses were introduced collinearly into the cell with the excitation pulse being optically delayed by 3 ns from the preparation pulse. The fluorescence around 546.2nm, corresponding to 6 $^3P_2$ – 7 $^3S_1$ transition, was sampled from the viewing port of the cell and was detected with a bandwidth of 8nm by a photomultiplier (Hamamatsu R-374) attached to a 20cm monochromator (Ritsu MC-20L) equipped with a 1200 grooves/mm grating blazed at 400nm.

Figures 1(a) and 1(b) show the fluorescence-excitation spectra of Hg*(6 $^3P_0$)-Ar and Hg*(6 $^3P_0$)-Ne plotted against wavenumber shift Δ (in cm^{-1}) from the 404.7nm line. The

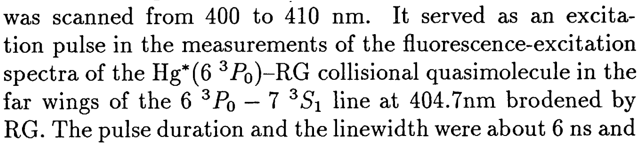

Figure 1. Fluorescence excitation spectra observed at the $E\ ^31$ – $a\ ^30^-$ band of the (a) Hg*(6 $^3P_0$)–Ar and (b) Hg*(6 $^3P_0$)–Ne collisional quasimolecules. Δ = 0cm^{-1} denotes the 6 $^3P_0$ – 7 $^3S_1$ transition.

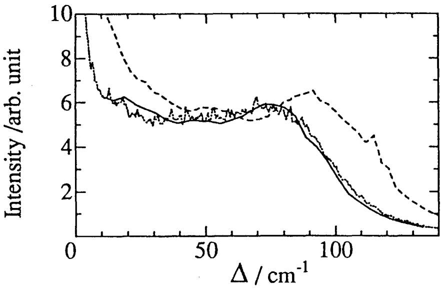

Figure 2. Measured and calculated blue-wing excitation spectra of Hg*(6 $^3P_0$)–Ar. The dotted line is the measured spectrum, the solid line represents the result calculated using the potential curves obtained in this study, and the dashed line represents the result calculated according to the potential parameters given by Duval *et al.*[3]

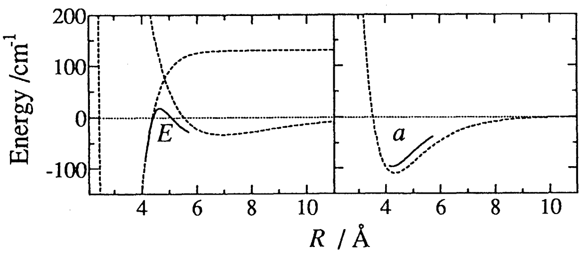

Figure 3. Comparison of the potential curves obtained in this study (solid lines) and by Duval *et al.* (dashed lines).[3]

Hg*(7 $^3S_1$)-RG state created by far-wing absorption correlates asymptotically to the dissociation limit of Hg*(7 $^3S_1$) + RG in the small $|\Delta|$ limit. The observed far-wing spectra are assigned to the transition between the E ^{31} and a $^30^-$ excited-states of the Hg–RG quasimolecules. The excitation spectra are highly asymmetric, with the blue wing far more extended than the red wing. A blue-wing satellite appears as a pronounced shoulder at $\Delta \sim 80$ cm^{-1} for Hg–Ar and 140 cm^{-1} for Hg–Ne. The observed blue-wing satellite arises from a maximum in the difference potential $\Delta V_{E-a}(R)$ between the E and a states. The origin of this maximum should be a hamp between the two potential wells of the double minimum $V_E(R)$, found for both Hg–Ar and Hg–Ne in the earlier laser-excitation studies on the vdW complexes.[3,7] It is seen in the figures that the satellite appears at larger $|\Delta|$s in the Hg–Ne system than in the Hg–Ar one. This is in consistent with the earlier vdW studies where the hump is found to be much higher for Hg–Ne ($\sim$ 150 cm^{-1})[7] than for Hg–Ar ($\sim$ 15 cm^{-1}).[3] One can also see a red-near-wing satellite at $|\Delta| \leq 20$ cm^{-1} for both Hg–Ar and Hg–Ne. This satellite is attributable to a minimum in $\Delta V_{E-a}(R)$, which appears because $V_E(R)$ is more attractive than $V_a(R)$ at larger R's ($\geq 8\AA$).[3] As is seen in the figures, the red-near-wing satellite is more close to the line core in the Hg–Ne system than in the Hg–Ar system, which is again reconcilable with the vdW results that the outer well is much shallower for Hg–Ne ($D_e \simeq 1.8$ cm^{-1})[7] than for Hg–Ar ($D_e \simeq 38$ cm^{-1}).[3] Thus one can recognize from the comparison of the two excitation spectra that a far-wing line profile is highly sensitive to the shape of the relevant potential-energy curves.

We have calculated the blue-wing spectrum of Hg–Ar according to the information on $V_E(R)$ and $V_a(R)$ given by Duval *et al.*[3] Since Duval *et al.* have not given the whole feature of $V_E(R)$, but has only given a hump-height (15 cm^{-1}) and the Morse parameters for each of the inner and outer potential-wells, we have constructed a single potential-energy curve $V_E(R)$ with the double-minima by joining two extended Morse potentials, $V_{E_1}(R)$ and $V_{E_2}(R)$, so that the resultant curve shows a hump of 15 cm^{-1} and agrees well with the potentials by Duval *et al.* at the inner and outer potential-wells:

$$V_E(R) = \frac{V_{E_1}(R)e^{-\alpha(R-R_{h1})}}{e^{-\alpha(R-R_{h1})} + e^{\alpha(R-R_{h1})}} + \frac{V_{E_2}(R)e^{-\alpha(R-R_{h2})}}{e^{-\alpha(R-R_{h2})} + e^{\alpha(R-R_{h2})}}, \tag{1}$$

where each extended Morse potential is given by

$$V_{E_i}(R) = a_i[e^{-\beta_{2_i}(R-R_{e_i})} - \frac{\beta_{2_i}}{\beta_{1_i}}e^{-\beta_{1_i}(R-R_{e_i})}], \tag{2}$$

with

$$a_i = D_{e_i}\frac{\beta_{1_i}}{\beta_{2_i} - \beta_{1_i}}, \qquad \beta_{1_i} = \sqrt{\frac{2\mu\omega_{e_i}x_{e_i}}{\hbar}}. \tag{3}$$

A small adjustment has been made on the shape of the hump so that a better agreement is achieved between the measured and calculated spectra. The values for the switching parameters in Eq.(1) are finally chosen as $\alpha = 0.75(\AA^{-1})$, $R_{h_1} = 4.4(\AA)$, and $R_{h_2} = 5.4(\AA)$, and the parameters used for the inner and outer Morse potentials, $V_{E_1}(R)$ and $V_{E_2}(R)$, are summerized in Table 1. Since the classical QST approach is not applicable to the satellite region, we calculated the far-wing spectrum using uniform semiclassical approximations for the free-free Franck-Condon factors. Details of the calculating procedure has been given elsewhere.[5] The result is shown by the dashed curve in Figure 2 and compared with the measured spectrum. It is seen in the figure that the calculated spectrum does not agree with the present experimental result. The calculated satellite appears at larger detunings than the measured one. We attribute this discrepancy to an inaccuracy of the $V_a(R)$ given by Duval *et al.*[3] We have modified $V_a(R)$ so that the better agreement is achieved between the calculated and measured blue-wing spectra. A simple Morse function was used for $V_a(R)$. We have found that the dissociation energy 97 cm^{-1} of $V_a(R)$, the value obtained by Fuke *et al.*,[4] gives the right position of the blue-wing satellite. The resultant calculated spectra is shown by the solid curve in Figure 2, and the Morse parameters finally chosen for $V_a(R)$ are summarized in Table 1. As is seen in the figure, a satisfactory agreement is obtained between the calculated and measured spectra. $V_E(R)$ and $V_a(R)$ thus obtained in this study are plotted in Figure 3 and compared with those given by Duval *et al.*[3] It is clearly seen in the figure that $V_a(R)$ has been improved substantially in this study. It is important to note that the $E \rightarrow a$ emission spectra measured by Duval *et al.*[3] is well reproduced also by the potential curves obtained in this study.

The similar analyses of the potential curves for Hg–Ne are now in progress.

References and Notes

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