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Synthetic Metals 140 (2004) 109–111
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Commentary

Comments on the paper "Modulation of period of quantum beats from optical emissions from the excited electronic states of mercury triatomic clusters" by E. Sarantopoulou, et al. (Eds.) [Synth. Met. 124 (2001) 267]

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Received 17 June 2003; received in revised form 22 September 2003; accepted 21 October 2003

In this paper, a molecular beam apparatus is presented and Sarantopoulou et al., claimed that they observed mass spectra assigned to the Hg_3^{2+} cluster, formed in their apparatus. Moreover, they observed modulated optical emissions, interpreted as quantum beats ("QB"), stemming from such excited clusters. In the following, arguments will be presented that speak against the formation of such clusters and the interpretations of Figs. 1 and 2 given by the authors.

1. The experimental results stem from two different experimental arrangements: an "old" cell experiment [1,2] revealed Fig. 2 and a "late" *molecular beam* experiment [3] revealed Fig. 1.

   The experimental apparatus is described clearly in the paper's Section 2/lines 1–13: for any reader, it follows unambiguously that the molecular beam apparatus incorporates two diagnostic systems: one for optical signal processing with which the "quantum beat" signal, Fig. 2, was recorded and a mass spectrometer to record the mass spectrum, Fig. 1. There is no evidence that Fig. 2 was detected by a "visible" PMT, as the authors claim in their reply. This was *nowhere* presented explicitly in this paper. In order to gain more insight: an explicit reference to a "visible" EMI 9829 PMT was made only in [1] and this supports my argument that Fig. 2 was recorded in that "old" cell experiment and not in the present molecular beam experiment. This argument is further supported by Part II in [3]: in Chapter 1, a cell experiment was presented, revealing the "quantum beat" signal. In Chapter 2 the molecular beam apparatus was described, where *only mass spectra* were recorded and Hg_3 formation was described by the same mechanisms as in the previous cell experiments.

   To summarize, the authors' reply is both irrelevant and confusing: from the above discussion it is clear that Fig. 2 is a 1986 result [1] that is re-published in a 2001 paper!
2. Fig. 2 cannot be attributed to a quantum beat signal, originating from Hg trimmers.

   According to the authors' model (Fig. 1 of their reply), two 157 nm photons are required for the Hg_2 and Hg_3 formation. In the "old" cell experiments [1,2], *an unfocused* 157 nm laser beam was sent into the $HgBr_2$ vapor cell. Typical excimer transitions have a few nm spectral width while the beam has a ca. 20 mm × 8 mm rectangular shape. Furthermore, molecular transitions are generally weaker than atomic ones, since the oscillator strength is distributed into many rotational-vibrational transitions. Under these experimental conditions, only *one-photon* absorption would be possible in that cell experiments. Indeed, their Fig. 2 in [2] was a laser-induced emission spectrum, assigned to HgBr C → X transitions that followed a single photon excitation of $HgBr_2$. This was a quite reasonable but trivial result!

   Similarly, the observation of emission spectra and their definite assignment to Hg ("precursor" species for Hg_3 in their model) and Hg_3 itself would be the best proof for the validity of their model. For Hg the authors presented the "bargraph" (four bars drawn by hand!) in Fig. 7 of [1] giving only relative Hg line intensities: it is not a spectrum recorded in the usual sense (no line-width, no baseline). For Hg_3 spectra they presented Fig. 5 in [2]: the solid line is obviously drawn by hand: they have not given a single *peak* assignment to interpret it as an Hg_3 emission! Such "spectra" constitute a *very poor* experimental evidence for the Hg_3 formation under the authors' experimental conditions. Furthermore, a

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0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2003.10.019

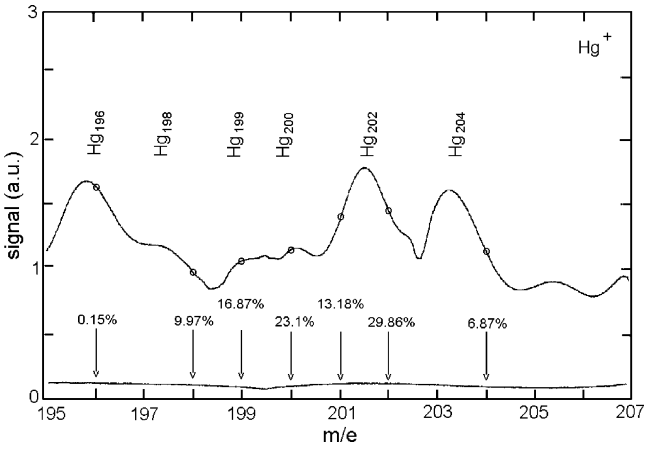

Fig. 1. Hg^+ mass spectrum, after photo-ionisation of $HgBr_2$ with 193 nm.

two-photon experiment would require a quadratic laser intensity dependence of the Hg and Hg_3 signals. No such results have ever been presented in [1,2].

Referring to the work of Shigenari et al. [5]: a *focused* 193 nm laser beam was used and according to a three-photon absorption, $HgBr_2$ was photo-dissociated and strong atomic Hg emissions were recorded, from the *same* Hg 6^3P metastables as in the present authors' model. *No* Hg_2 and Hg_3 molecules were observed in [5], although those conditions were more favourable, due to the higher working vapour densities. Although [5] is closest to the authors cell experiments [1,2], it is *systematically* ignored throughout their reply, obviously because [5] does not support their model for the trimmer formation! Furthermore, [5] contradicts with the authors claim "... the formation of the Hg atoms is a process which depends on the wavelength of the laser and not of its intensity." Instead, they made extensive use of literature data, where extremely different conditions (cells with pure Hg vapour) prevailed!

Although the Hg_3 formation proved *speculative* above, I refer to the "QB" only for completeness: the emission signal of a single particle is obviously so weak that cannot be observed. QB-spectroscopy is based on a coherent superposition of signals from all emitting particles (*inter*molecular coherence), induced by the laser. The "QB" signals are always recorded in a resonant excitation/de-excitation process, such that coherence-destroying mechanisms (LIF or collisions) are avoided. The authors' model is nothing but another *intra*molecular mechanism, such as the fine and hyperfine structure, Λ-doubling, etc. leading to energy level splitting, a common phenomenon in atomic or molecular systems. The authors have therefore depicted the *wrong* textbook in trying to attribute the modulated optical signals to "QB".

As a result, both the authors' model for the Hg_3 formation and the "QB" observation *collapse* due to the lack of reliable experimental evidence and the author's misunderstanding of the "QB"-spectroscopy principles, respectively.

3. Fig. 1 is not indicative for a Hg_3 formation in the authors' molecular beam.

To account for their "observation" of the Hg_3, the authors developed a new theory ("explosive dissociation") that was neither in [3] nor in their original paper [4] mentioned before. Not a single referred publication is presented either. This "theory" might be applicable in experiments, where pressure and density values exceed the corresponding conditions of the authors' experiment by orders of magnitude. Within this theory, the authors estimated the metastable Hg density in the interaction region to be $10^{19}/cm^3$ s. But in [3] the same quantity was estimated to be only $10^{12}/cm^3$ s! A difference of seven orders of magnitude cannot speak for a sound "theory"! Moreover, this "explosive dissociation" is proposed only *after* my comments and I will therefore disregard it.

Since the molecular beam results have not been published before, my arguments below stem directly from the authors' primary experimental data. In [3] they focused a 193 nm laser beam with a 20 mm MgF_2 lens on an $HgBr_2$ beam and recorded a mass spectrum in the $e/m = 195$–207 range, see Fig. 1. I inserted into this signal the percentages of the natural abundances of the Hg isotopes from the literature: the recorded spectrum does not reflect the expected Hg natural abundances. First, the ^{196}Hg (0.15%) signal is stronger than the ^{199}Hg (16.87%) and ^{200}Hg (23.1%) ones. Secondly, the peaks of the mass signal do not correspond to the expected positions of the Hg isotopes on the mass scale. Third, in [3] is claimed that a strong signal was observed at $e/m = 202$ and zero ("noise level") elsewhere. Since no enriched $HgBr_2$ was used, this contradicts with the broad and continuous signal recorded. Fourth, the authors performed an intensity dependence measurement of the Hg^+ signal ($S \sim I^n$) to extract the number n of photons needed to ionise Hg: they proposed two possible four-photon mechanisms for the Hg ion production. But their measurements revealed $n \sim 1.98$ from for laser intensity values in the non-saturated region. This Hg^+ mass spectrum is therefore very poor experimental evidence that Hg^+ has ever been detected. Furthermore, it contradicts the authors' own argument that "... the formation of the Hg atoms is a process which depends on the wavelength of the laser and not of its intensity", meaning that a 157 nm laser can produce Hg metastables but a 193 nm one not!

Turning to trimmer formation with a 157 nm laser beam, we note that a similar mass spectrum of the "precursor" Hg^+ for 157 nm was never reported! Instead, the authors presented in [3] an Hg_3^{2+} mass spectrum, part of which is Fig. 1 in their paper [4]. Taking into account (i) the poor experimental evidence of Fig. 1 to be a Hg^+ mass spectrum for 193 nm and (ii) the authors' claim in their reply that "... the estimated density of the dissociated Hg atoms ... is six–seven orders of

magnitude higher than the Hg_3 clusters", I concluded that Hg_3^{2+} cannot be detected by the authors' apparatus. This is again supported and reinforced by the mass spectrum in Fig. 1 of [4], in respect to the Hg natural isotope abundance: for example, a trimmer formed by three (the least abundant) ^{196}Hg isotopes would be detected at $e/m = 294$. The most abundant and still detectable trimmer ($^{200}Hg+^{200}Hg+^{199}Hg$) is expected at $e/m = 299.5$. The latter should be by a factor of 10^6 more abundant than the trimmer at 294. But according to Fig. 1 [4], the signal at 299.5 is only ca. 30% higher than that at 294.

The authors' arguments about the Hg_3^{2+} stability and formation, based solely on literature data from experiments where different experimental conditions prevail, are irrelevant and contribute nothing to the present discussion. Since the stability of multiple-charged clusters is a sensitive function of the number of their electrons, it is a real speculation to draw conclusions for the cluster stability, based only on the properties of the Mg_3^{2+} ion. The question about the double ionisation mechanism, being either a direct, one-step or indirect, two-step (via the singly ionised cluster) process, can be answered, e.g. by recording the Hg_3^{2+} signal dependence on the 157 nm laser beam fluence (log–log plot). Such a measurement was never done. I consider it as rather impossible, due to the low experimental confidence of Fig. 1 [4] to be an Hg_3^{2+} spectrum as well as to the lack of necessary knowledge of the trimmer structure.

To summarize: the authors' arguments for trimmer synthesis *collapse* due to the poor quality of their own experimental data.

As a final conclusion, the Hg_3^{2+} formation under the authors' experimental conditions does not follow necessarily from their presented experimental data. Their model for the trimmer formation is rather a speculation and the modulated signals contradict the principles of the "QB"-spectroscopy.

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