

Comment on "Coupling to Dipole Forbidden Modes: CO on Pt(111) Studied by Infrared Spectroscopy"

In a recent Letter Engström and Ryberg (ER) reported the detection of a Fermi resonance (FR) of a diatomic adsorbate species (CO) adsorbed on Pt(111) [1]. According to their interpretation, the contributing component modes are the Pt-CO stretching mode $\nu_{\text{Pt-CO}}$ (385 cm^{-1}) and the (difference) combination band of frustrated translation (510 cm^{-1}) minus frustrated rotation (133 cm^{-1}). Four different isotopic CO species have been examined, but only for regular $^{12}\text{C}^{16}\text{O}$ is a doublet observed and attributed to Fermi resonance coupling. This interpretation was inspired by a theoretical study of Burke *et al.* [2] which discusses the occurrence of a FR of the metal-CO stretch mode and the (sum) combination band of the abovementioned frustrated bands. A major subject of Ref. [2] was the continued lack of detection of the predicted FR in the experiments which ER now seem to have put to an end. However, the presented evidence is not convincing and more importantly is contradictory, as will be outlined in the following.

Fermi resonances are well-known distortions in vibrational spectroscopy and can be classified as avoided crossing phenomena of sublevels with identical symmetry properties [3]. As a result of this coupling the character of the individual modes changes; the extent of the mixing depends on the relative strength of the interaction as compared to their spectral separation. Two experimental observations are commonly related to FR mixing of modes: (a) an intensity gain of the (usually) weak combination band and (b) a frequency shift of both component modes, one shifting upwards and the other downwards in frequency, thereby giving the impression of an apparent repulsion of the two bands forming the Fermi resonance. In the work of ER, condition (a) seems to be fulfilled for the regular CO isotope (for the others the frequency matching may not be close enough so that the combination band might be undetectable), and an approximate 1:1 intensity ratio of the doublet may indicate a rather strong coupling, i.e., without the FR coupling $\nu_{\text{Pt-CO}}$ and the combination mode would possess approximately the same resonance frequency [3]. Looking at the $\nu_{\text{Pt-CO}}$ isotopic frequency shifts $^{12}\text{C}^{16}\text{O} \leftrightarrow ^{13}\text{C}^{16}\text{O}$, as compared to $^{12}\text{C}^{18}\text{O} \leftrightarrow ^{13}\text{C}^{18}\text{O}$, then 7 cm^{-1} is derived in *both* cases. This means that, for regular CO, Engström and Ryberg observe no FR-induced frequency shift at all (a FR-induced blueshift of $\nu_{\text{Pt-CO}}$ by $2-3 \text{ cm}^{-1}$

would be expected) [4]. Likewise, for the isotopic shifts $^{12}\text{C}^{16}\text{O} \leftrightarrow ^{12}\text{C}^{18}\text{O}$, as compared to $^{13}\text{C}^{16}\text{O} \leftrightarrow ^{13}\text{C}^{18}\text{O}$, an equal splitting of 16 cm^{-1} is obtained. It is therefore obvious that the FR coupling superimposes a zero frequency shift on the $\nu_{\text{Pt-CO}}$ mode of $^{12}\text{C}^{16}\text{O}$ even though the observed 1:1 intensity ratio suggests a strong coupling. As both features, the intensity gain and the frequency shift, are naturally interrelated they must occur in common, which clearly is not the case.

A second issue needs to be raised as well: ER suggest that a *difference* combination mode is responsible for the Fermi resonance which requires thermal excitation of the low frequency component at 133 cm^{-1} . The experimental conditions ($T_{\text{meas}} = 100 \text{ K} \approx 70 \text{ cm}^{-1}$), however, would impose a rather low thermal population probability $p \leq 0.2$ which contradicts the found 1:1 intensity ratio of the "Fermi resonance doublet." Also a pronounced temperature dependence is expected. Unfortunately, ER did not inspect the temperature dependency which could establish important additional evidence in favor of or against the suggested interpretation as a FR. Taken together, the interpretation of the extra band in $^{12}\text{C}^{16}\text{O}/\text{Pt}(111)$ spectra to be an indication for a Fermi resonance appears unlikely, and other explanations should be envisaged.

I want to mention in closing that I have observed recently a clearcut case of a Fermi resonance with component modes according to Ref. [2] which fulfills all of the abovementioned conditions [5].

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- [2] K. Burke, D.C. Langreth, M. Persson, and Z. Y. Zhang, Phys. Rev. B **47**, 15 869 (1993).
- [3] G. Herzberg, *Molecular Spectra and Molecular Structure II; Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1945).
- [4] The slightly dissimilar $\nu_{\text{Pt-CO}}$ resonance frequencies of the various CO isotopes would affect the quoted splittings only to within 5% and are negligible. Besides, consideration of this effect would aggravate the disagreement.
- [5] P. Jakob (to be published).