Comparative study of $^1\Sigma_u^+$ and $^1\Pi_u$ excitations of carbon dioxide by high-resolution inelastic x-ray and electron scattering

Dong-Dong Ni*, Long-Quan Xu*, Ya-Wei Liu* and Lin-Fan Zhu * [1]

* Hefei National Laboratory for Physical Sciences at Microscale, Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Synopsis The inelastic squared form factor(ISFFs) for valence electronic states $^1\Sigma_u^+$ and $^1\Pi_u$ of carbon dioxide have been derived from electron energy loss spectra measured at an incident electron energy of 1500 eV and inelastic x-ray scattering(IXS) method at an impact photon energy around 10 keV. The ISFFs obtained are then compared with the previous EELS results and theoretical calculations.

Carbon dioxide is one of the fundamental constituents of the planetary atmosphere. The molecule also plays an important role in laser technology, gaseous discharges, and low-temperature plasma devices. Furthermore, carbon dioxide is one of the simplest polyatomic molecules, thus its study is also of particular interest from the viewpoints of molecular spectroscopy[1].

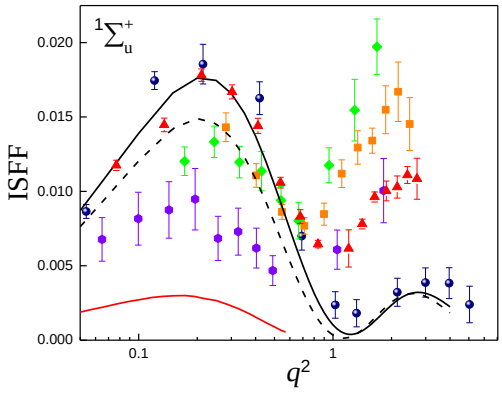

FIG. 1 The dots are the present IXS results. The EELS results are: hexagons 200eV[2], diamonds 300eV[3], squares 500eV[3] and triangles 1500eV of this measurment. Red thin line: theoretical calculation by Buenker *et al.*[4].The black solid line: theoretical calculation by Watanabe *et al.*[1] within vibronic effects. The dash line: theoretical calculation by Watanabe *et al.*[1] without vibronic effects.

As shown in FIG.1, the significant role of the vibronic effects are manifested through the comparison between the calculation by taking equilibrium geometry and the one by taking the vibronic effects into consideration. It can be seen clearly that the theoretical calculation by Watanabe *et al.* [1] which takes the vibronic effects into account satisfactorily reproduce the present IXS results.

It is clear in FIG.2 that there is no appreciable difference between the equilibrium geometry and vibronic effects calculations. The calculation by Watanabe *et al.* [1] seems to slightly underestimate the measured IXS result, however the overall shapes are in reasonably good agreement with each other.

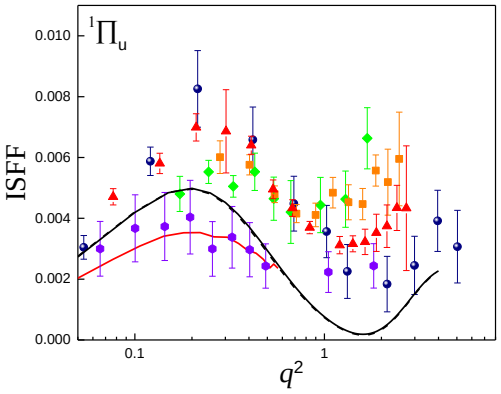

FIG. 2 Same as FIG.1. The black solid line and dash line coincide over the whole momentum transfer squared region.

By comparing the present experimental results with preceding EELS outcomes and theoretical calculations, some meaningful conclusions can be reached. The vibronic effect plays an important role in reproducing the experimental ISFF profile of $^1\Sigma_u^+$ satisfactorily. Despite its significant role in the transition to state $^1\Sigma_u^+$, vibronic effect is negligible for the transition $^1\Pi_u$. The discrepancies between IXS and EELS results over the whole range suggests the breakdown of the first Born approximation (FBA) even at impact electron energy of 1500 eV.

References

[1] N. Watanabe, T. Hirayama, D. Suzuki et.al., 2013 *J. Chem. Phys.* **138** 184311.
[2] M. A. Green, P. J. O. Teubner, L. Campbell et.al., 2002 *J. phys. B* **35** 567.
[3] K. N. Klump and E. N. Lassettre,1978 *J. Phys. Chem. Ref. Data* **14 215**.
[4] R.J.Buenker, M.H.Honigmann, H. P. Liebermann et al., 2000 *J. Chem. Phys.* **113** 1046.

[1] E-mail: lfzhu@ustc.edu.cn