

Supplementary Information

Vibrational Spectra of the Ruthenium-tris-Bipyridine Dication and its Reduced Form in Vacuo

Musleh Uddin Munshi^a, Jonathan Martens^a, Giel Berden^a, Jos Oomens^{a,b*}

^aRadboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

^bUniversity of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands

e-mail: j.oomens@science.ru.nl

Table S1 Calculated average Ru—N distances (Å) and Ru centered bond angles (°) of [Ru(bpy)₃]²⁺ and [Ru(bpy)₃]⁺ ions in the gas phase compared with crystallographic literature data.¹ The TZ2P basis set is used with all three functionals. Atom labels are shown in Figure 2. Parenthesized values are standard deviations in units of the last quoted digit.

Parameter	[Ru(bpy) ₃] ²⁺				[Ru(bpy) ₃] ⁺		
	B3LYP	O3LYP	M06	Exp (X-ray crystallography)	B3LYP	O3LYP	M06
d(Ru—N)	2.095(0)	2.002(0)	2.097(0)	2.065(2)	2.092(0)	2.017(0)	2.069(0)
Bond angle (°)							
∠N-Ru-N'	78.2(0)	79(0)	77.8(0)	78.7(1)	78.3(0)	78.8(0)	78.4(0)
∠N-Ru-N''	87.2(0)	88.5(5)	89.2(1)	89.1(1)	88.1(0)	89.7(2)	90(2)
∠N-Ru-N'''	174.0(0)	173.6(4)	172.4(0)	173.0(1)	173.5(1)	172.6(3)	172.1(2)
∠N'-Ru-N''	96.7(0)	96.4(3)	96.7(0)	96.3(1)	97.0(0)	96.0(2)	96.0(1)

1. Rillema, D. P.; Jones, D. S.; Woods, C.; Levy, H. A. *Comparison of the Crystal Structures of Tris Heterocyclic Ligand Complexes of Ruthenium(II)*. *Inorg. Chem.*, **1992**, *31*, 2935-2938.

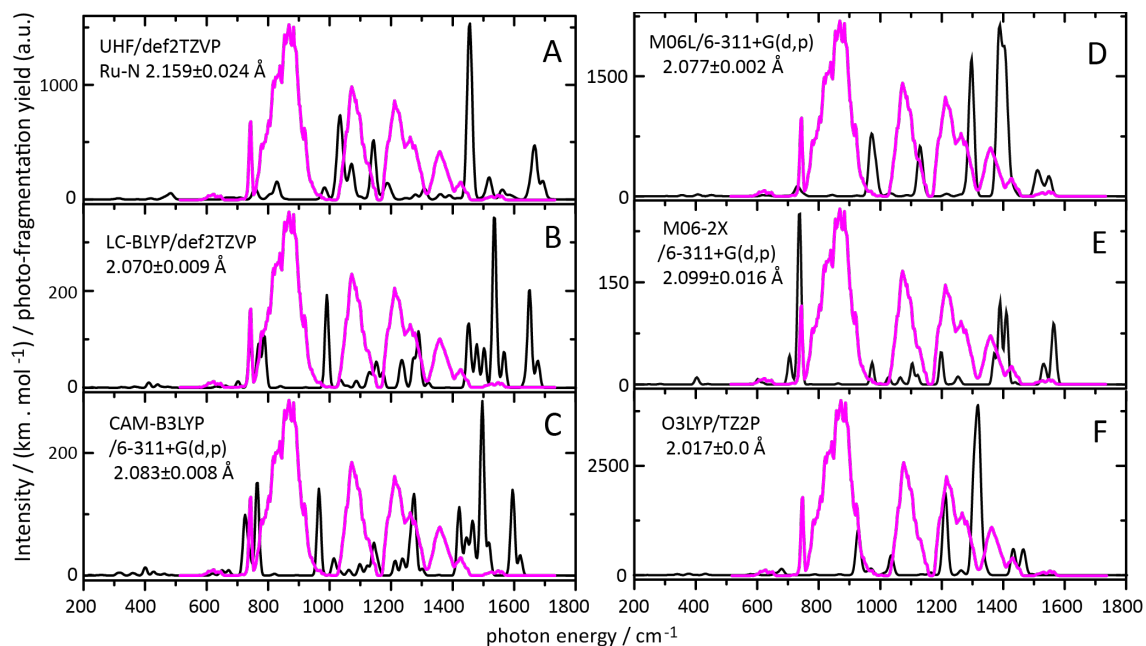


Figure S1 Theoretical IR spectra for $[Ru(bpy)_3]^+$ at additional levels of theory compared with the experimental IRMPD spectrum (magenta trace) for the charge-reduced complex ion. The corresponding geometries (not shown) are in all cases hexa-coordinated. The average Ru-N bond distance is indicated for each calculation.