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TEMPORARY NEGATIVE ANIONS OF PARA-BENZOQUINONE

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ABSTRACT

We present detailed *ab initio* scattering calculations for electron collisions with *para*-benzoquinone. The R-Matrix method has been used to study elastic and electronically inelastic scattering. We have identified 26 resonances of Feshbach, core-excited shape and mixed character between 0 and 8 eV. Agreement of our resonance spectrum with existing literature is presented. Integral elastic and total inelastic cross sections are also presented. These calculations have enabled us to investigate the resonance spectrum of *p*-BQ in greater detail than ever before.

INTRODUCTION

para-Benzoquinone is the prototypical member of the quinone's family, playing a crucial role in electron transfer reactions in chemistry and biology, for example in photosynthesis¹. Some of their derivatives present antitumoral activity² whilst other are involved as cofactors in quinoenzymes³. A lot of experiments and calculations have been performed but no consistency was found between the published data – see table 1, although there were not proper scattering calculations available

We showed that there is a great dependence of the anionic states on the molecular geometry, in agreement with previous photodetachment studies.⁴

The emphasis of this work is the identification and characterization of the shape and core-excited resonances.

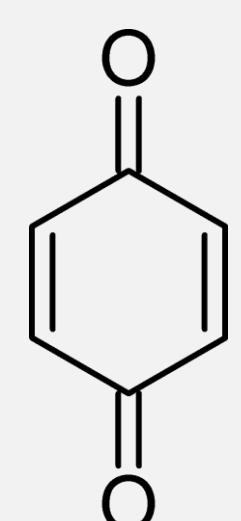


Figure 1. Chemical structure of *para*-benzoquinone.

R-Matrix⁵

$$\Psi_k^{N+1} = \mathcal{A} \sum_{i=1}^n \sum_{j=1}^{n_c} \Phi_i(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}; \sigma_{N+1}) \frac{u_{ij}(r_{N+1})}{r_{N+1}} a_{ijk} + \sum_{i=1}^m \chi_i(\mathbf{X}_{N+1}) b_{ik}$$

We used **UKRmol** suite, the computational implementation of the R-Matrix method. It consists on the division of the molecular space into two regions:

- The inner region, where correlation and exchange effects between all electrons have to be considered;
- The outer region where those effects can be neglected.

The most challenging step is the diagonalization of the Hamiltonian to get the eigenvalues and all the calculations are performed using the fixed nuclei approximation.

- Spin and space coordinates of all N/N+1 electrons;
- Spin of the scattering electron;
- Radial and angular coordinates of the scattering electron;
- Describes the *i*th electronic state of the N-electron target;
- Radial part of the wave function of the scattering electron;
- L² integrable functions describe the short-range polarization-correlation effects.

RESULTS

Static-Exchange Plus Polarization (SEP) and Close-Coupling (CC) calculations were performed. The first describes the polarization effects well, being a good method to describe the shape resonances. On the other hand, the CC method includes the electronically excited states, suitable to describe the core-excited resonances.

We also used the time-delay technique to find the resonances as it allows the identification of the ones that are overlapped.

Table 1. Positions and widths (in brackets) in eV, of the six low-lying resonances of *p*-BQ calculated at the SEP and CC level. The capital letters mean: Char – Character; S – shape resonance; F – Feshbach resonance; M – mixed shape-Feshbach resonance.

Sym.	E _k (Width)		Char.	Cheng ⁶	West ⁷	K&B ⁸	Amérigo ⁹	Honda ¹⁰	Experiments
	SEP	CC							
1 ² A _u	0.85 (0.012)	1.10 (0.030)	S	0.910 (S) (0.346)	1.01 (S)	0.56 (S)	0.91 (S)	0.83 (S)	1.35 ¹¹ , 1.43 (S) ¹² , 1.60 (S) ¹³ , 1.41 ¹⁴
1 ² B _{2u}	-	1.70 (8E-4)	F	1.136 (F) (0.014)	1.03 (F)	0.68 (F)	0.96 (F)	1.22 (F)	-
1 ² B _{3g}	-	1.75 (0.001)	F	0.956 (F) (0.042)	~ 0.9	0.7 (F)	0.87 (F)	1.09 (F)	-
1 ² B _{3u}	1.96 (0.159)	1.90 (0.071)	S	1.587 (M) (0.351)	0.68 (S)	1.43 (M)	1.31 (M)	1.79 (S)	0.70 ¹¹ , 0.72 (S) ¹² , 0.77 (S) ¹³ , 0.69 ¹⁴
1 ² B _{1g}	3.05 (0.007)	2.35 (0.007)	M	2.099 (M) (0.058)	-	1.73 (F)	1.99 (F)	2.66 (F)	-
2 ² B _{3u}	3.36 (0.058)	2.67 (0.138)	M	2.332 (M) (0.139)	1.86 (F)	2.14 (F)	1.87 (M)	2.44 (F)	1.90 ¹¹ , 2.15 (S) ¹² , 2.0 (S) ¹³

Details of the calculation:

- ✓ Radius 13a₀
- ✓ Basis set: cc-pVDZ
- ✓ Deletion Threshold 10⁻⁷
- ✓ Partial waves 4
- ✓ 48 electronically excited states – up to 9.4 eV on CASSCF calc.
- ✓ 8 states averaged - CASSCF

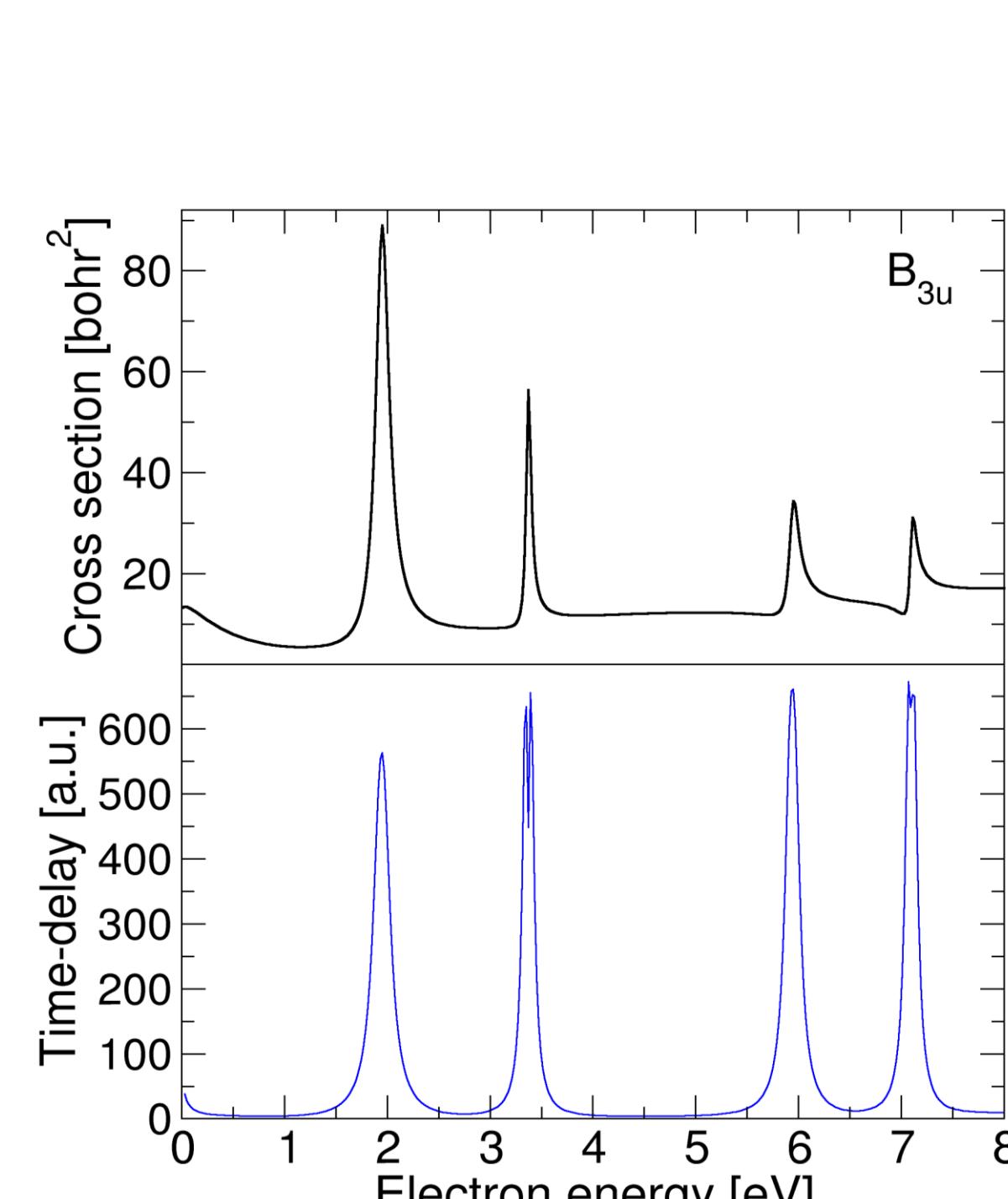


Figure 2. Example of the cross section for the B_{3u} irreducible representation (upper panel) and respective time-delay (lower panel), both at the SEP level. It's possible to observe the same four peaks in each one.

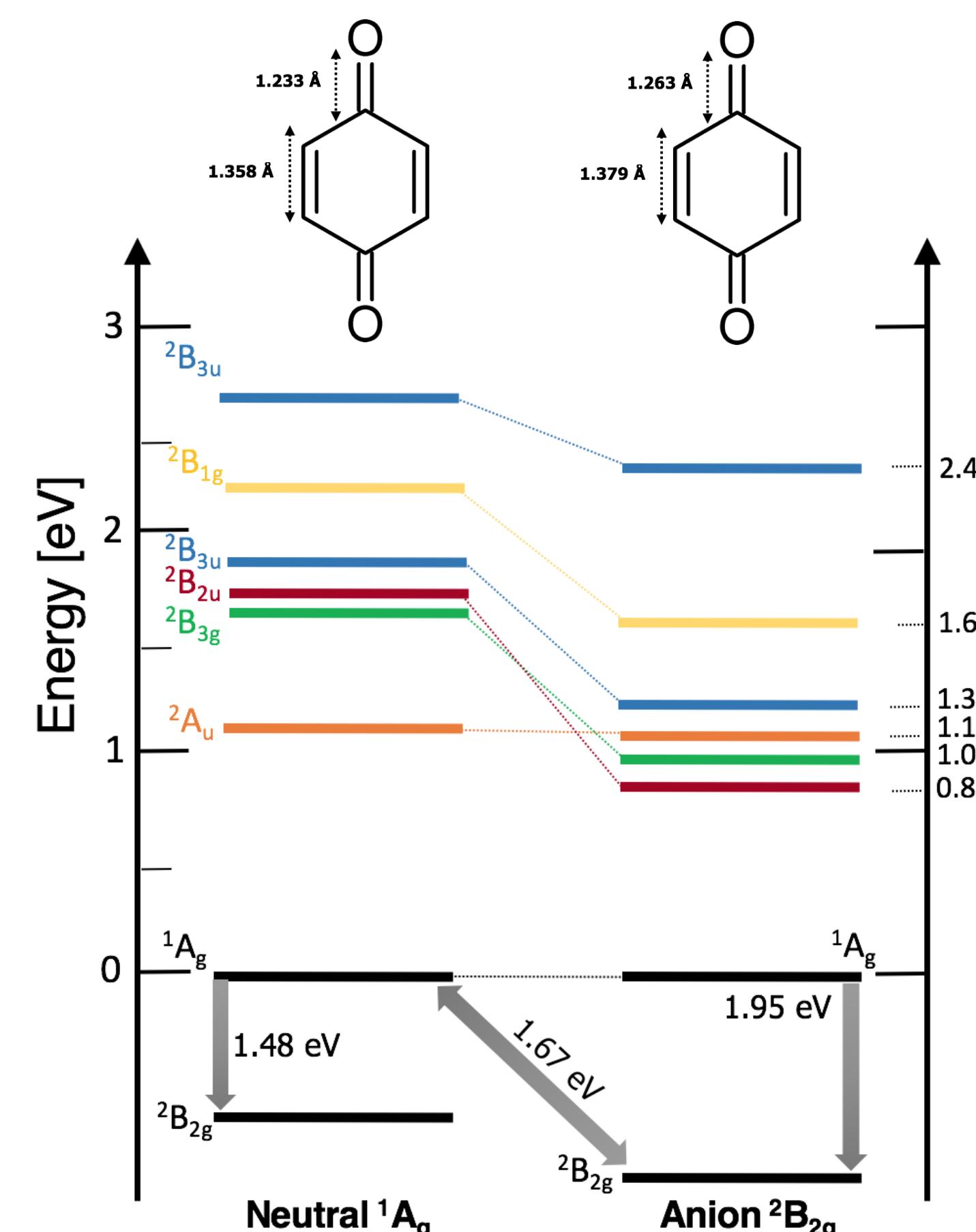


Figure 3. Resonance energies for *p*-BQ using its neutral and anion geometry. The main differences are in the bonds associated with the π orbitals.

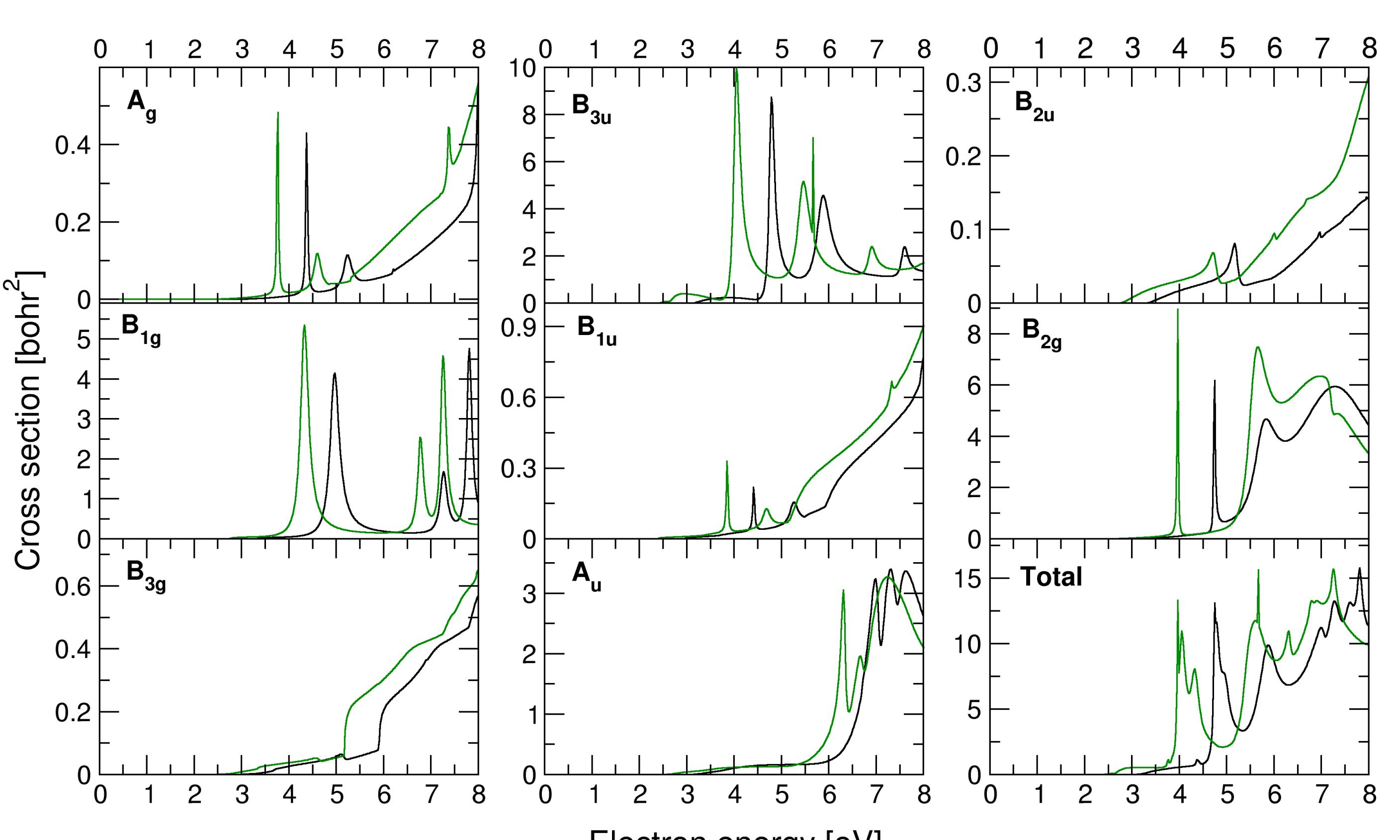


Figure 4. Total inelastic cross sections for the neutral geometry of *p*-BQ (black line) and for the anion geometry (green line).

These figures illustrate the differences on the resonance positions when the bond length is changed – even for just 0.03 Å. For the six low-lying resonances, there are the swapping of some resonances, demonstrating that the shifting is not the same for all resonances. For higher energies, the shifting is more consistent. Although no new resonances were found for these different geometries, the shifting can be ~1eV, which show the peculiarity of this system.

CONCLUSIONS

- We have identified a large number of resonances, mainly of core-excited and mixed character;
- Most of these resonances appear above 4 eV, in the same energy region as a large number of excited states of p-BQ.
- The six lowest resonances are in good agreement with the published data. These resonances are energetically very close (roughly within 1.5~eV) and their order around the equilibrium geometry of the neutral molecule is very sensitive to small changes in bond lengths. This ordering, or more generally the relative position of the resonant states, has implications for the photodetachment process.
- Further work, particularly experimental electron scattering measurements (e.g. electron energy loss spectroscopy and velocity map imaging experiments), could contribute to elucidating the details of the resonant spectrum for this very interesting and fundamental molecule.
- Future theoretical work is being carried on the *p*-BQ-H₂O complex: action spectroscopy experiments¹⁵ on *p*-BQ and *p*-BQ-H₂O complex have indicated that hydrogen bonding with one water molecule seems to have little effect on the photodetachment processes.

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