CROSS SECTIONS FOR SCATTERING OF ELECTRONS ON BF_3

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Abstract. We calculate cross sections for elastic scattering and electronic excitation of BF_3 molecules by low energy electrons. The R-Matrix code Quantemol-N has been used for calculations. The cross sections indicate the presence of a shape resonance of symmetry B_1 (A_2" in D_{3h}) at around $4.5\,eV$.

1. INTRODUCTION

Collisions of electrons with atoms and molecules represent the interaction that determines the behaviour of plasmas. Therefore, studying electron scattering has attracted considerable attention over the years (see e.g. Morrison 1983). Boron trifluoride (BF_3) is used in instruments such as neutron counters (Chen and Chung 1997) and in plasma doping (Radovanov 2005). The importance of further optimization of plasma doping sources dictated the need for the present study as measured properties of discharge afterglows and discharge periods require more direct modeling.

This work dealing with BF_3 is focused on computing the total (integrated) electron scattering cross-sections. This data will enable more accurate calculation of the transport coefficients. Whereas to date there has been no theoretical study on this topic, the most recent experimental enquiry was that of Szmytkowski et. al. (2004).

The R-matrix method has already been successfully applied to a number of molecules, including CF_3 (Rozum et al. 2003), NH_3 (Munjal and Baluja 2006) and O_3 (Gupta and Baluja 2005). Here we employ the Quantemol-N system developed at UCL (Tennyson at al. 2007)

2. THE R-MATRIX METHOD

The molecular R-matrix method (Burke and Berrington 1993, Burke and Tennyson 2005) is a variational technique that relies on the partitioning of configuration space into an inner and an outer part. The boundary is a sphere whose center is located at the center of mass of the molecule. The radius is chosen so that the molecular electron cloud is fully contained within the sphere (here $a = 10a_0$). In the inner

region, exchange and electron-electron correlations are considerable. As a result, the collision problem within a finite volume can be treated as a molecular bound state problem, by constructing and diagonalizing a Hamiltonian matrix. To meet the boundary conditions, the Bloch operator (Bloch 1957) is added to the diagonalized inner region Hamiltonian. In the outer (asymptotic) region, exchange and electron-electron correlations are not considered to be important, and one need only account for the long-range multi-polar interactions between the scattering electrons and the target. Hence the problem can be reduced to solving a set coupled second order equations, which is in practice done by propagating the R-matrix and matching to the asymptotic expansion of the solution (Morgan et al. 1998) to obtain the scattering observables.

In the inner region the scattering wavefunction Ψ_k^{N+1} is expressed through a close-coupling (CC) expansion:

$$\Psi_k^{N+1} = A \sum_i \psi_i^N(x_1, x_2, \ldots, x_n) \sum_j \kappa_j(x_{N+1}) a_{ijk} + \sum_l \chi_l(x_1, x_2, \ldots, x_{n+1}) b_{lk} \quad (1)$$

where A is the anti-symmetrization operator and $x_i = r_i \sigma_i$ is the spin-space coordinate of the i-th electron, ψ_k^N is the target wavefunction, κ_j is the j-th continuum orbital spin coupled with the scattering electron and χ_l are square integrable configurations in which all electrons are placed in target molecular orbitals (Varambhia and Tennyson 2007). Gaussian-type orbitals were used to represent the target molecular orbitals.

All these steps are now embedded within a package for general purpose calculations Quantemol-N, which was employed to carry out the calculations presented here.

3. RESULTS

The quantum chemistry and scattering models employed in the present work were automatically generated by the application. The calculations were carried out in the abelian C_{2v} sub-group of D_{3h}, the natural point group at the equilibrium geometry of BF_3 (NIST 2008).

Calculations were performed for BF_3 using Gaussian-type basis sets $6 - 311G^*$ and DZP. The configuration interaction method was used to construct the molecular (target) ground and electronically-excited state wavefunctions. The complete active space (CAS) involved freezing eight electrons in the $1a_1$, $2a_1$ $3a_1$ and $1b_2$ orbitals in all reference determinants, and allowing the remaining twenty-four electrons to be distributed freely among 4–$9a_1$, $1b_1$, $2b_1$, $3b_1$, 2–$5b_2$, and $1a_2$ molecular orbitals. A number of test calculations were carried out which retained an increasing number of target electronic states (closed channels) in the close-coupling expansion (1): 15, 48 and 56 states in both inner and outer regions. The scattering orbitals used by Quantemol-N were those appropriate for radius $a=10a_0$, where the partial wave expansion was up to and including g-wave. One virtual orbital was allocated to each symmetry where target orbitals were available. In the computation of the scattering observables the R-matrix was propagated to a radial distance of $100.1a_0$.

Quantemol-N generates graphs of cross section (Figure 1) and eigenphase (Figure 2). The calculation predicts the existence of a $^2B_1$ ($^2A_2$") shape resonance. The shape nature of the resonance was confirmed by the fact that it appeared in the basic
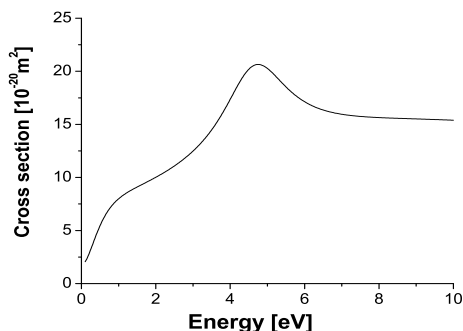
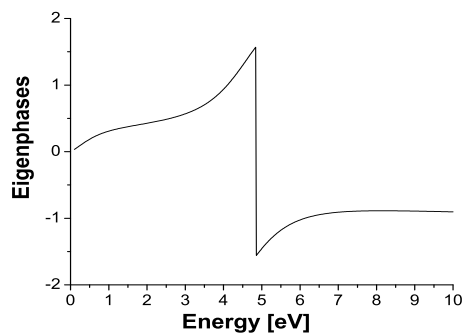Figure 1: Cross sections for elastic scattering obtained by the 48-state close-coupling calculation for BF$_3$.

Figure 2: ^{2}B$_1$ (^{2}A$_2$") eigenphases from the 48-state close-coupling calculation for BF$_3$.

1-state static exchange (SE) calculation, which is not discussed in the present work. The resonance obtained at above 4.5 eV has been observed experimentally but at a somewhat lower energy: 3.6 eV (Szmytkowski et. al. 2004). The latter of the two figures indicates more accurately the position of this resonance.

Results for the cross section were tested for convergence of the polarisation interaction by retention of more closed channels in expansion (1) and the outer region. Results obtained using 48 and 56 states appear to be almost identical and further changes do not appear to be likely. The parameters of the resonance yielded by these two computations differ considerably from the values obtained using only 15 states, as can be seen from Table 1. This is to be expected as there are markedly fewer closed channels retained.

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Table 1: Quantemol-N results for the positions and widths (in eV) of the resonance obtained by using different number of target states.

Resonance Parameter	15 states	48 states	56 states
E_r	5.09	4.56	4.56
Γ_r	1.65	2.17	2.18

Acknowledgements

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