If excitation transfers a molecule in a state containing more energy than the separated components, dissociation takes place (Fig. 1a). Above the dissociation limit, instead of discrete lines, a continuum is found as transnational motion is not quantized.

In some spectra, the line structure disappears already for energies below the dissociation limit but reappears again at higher energies. This finding is explained by a phenomenon called **predissociation** (Fig. 1b).

Predissociation is connected with an *internal conversion* from an excited state A towards a dissociative state B. We assume some relatedness between the vibrational states closely above the level of intersection and the transnational motion during dissociation. These circumstances allow a separation of a molecule via state B without supplying the energy of dissociation for state A. Note that, in the range beyond the blurred caused by predissociation, discrete lines are found. An interpretation would be that for higher vibrational states, a conversion towards state B is excluded again.

Sometimes, predissociation is introduced by additional external factors. For example, we can imagine a molecule to be pushed from state A to state B when colliding with another. Alternatively, under the influence of a field, selection rules are sometimes overridden. In such cases, we speak of collision- or field- **induced predissociation**.

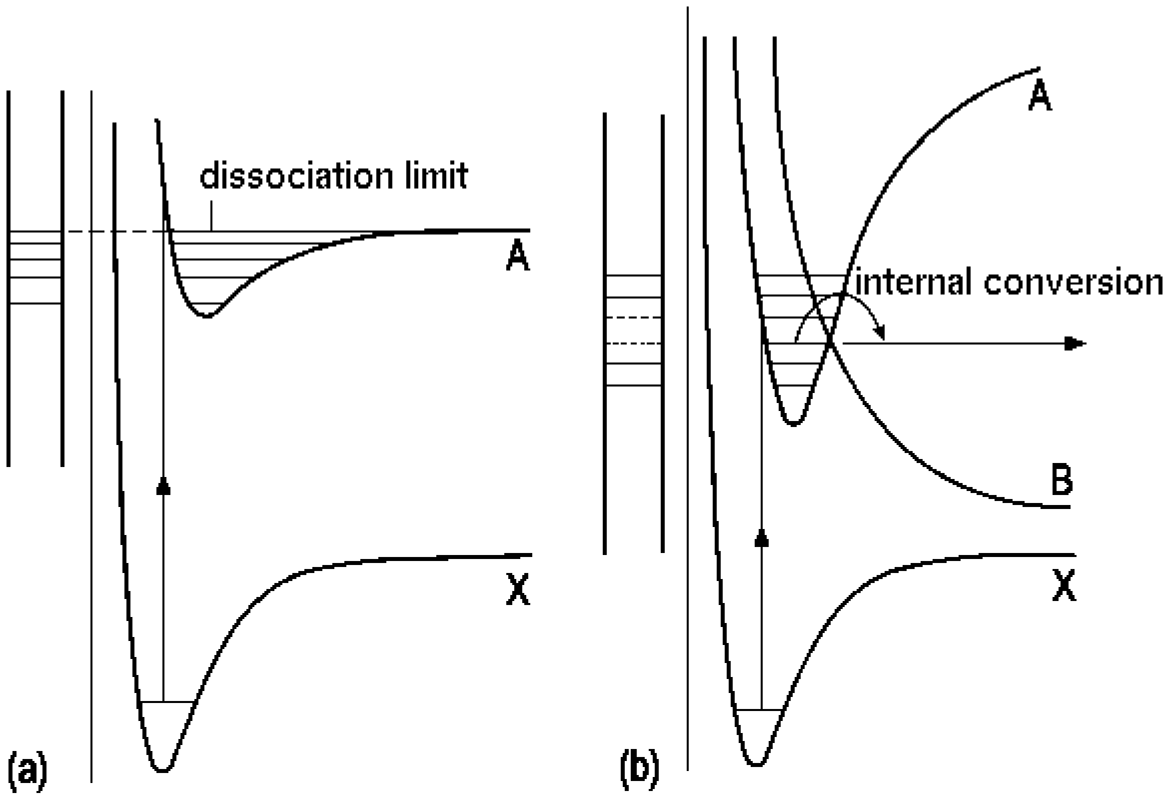


Fig. 1
a)In cases where an electronic excitation passes an amount of energy that lifts the molecule in a state above the highest vibrational levels, dissociation occurs. The respective spectrum displays a blurred zone beyond the so-called dissociation limit.
b)Predissociation is found for molecules where potential curves of a bound and an unbound state cross each other. An inferior amount of energy lifts the molecule in a state where the electrons can rearrange to an unbound state (internal conversion). In the spectral range that corresponds to these energies, a blurred zone appears. Beyond this zone, there are again discrete lines.

I. Cosby 1994 paper

All states , above the two lowest dissociation limits of N_2, N(S)+ N(S), and N(D) + N(S) are in principle subject to predissociation because they lie at energies above thee dissociation limits.
NOTE: This paper is photon dissociation , not electron impact dissociation
Cosby states :

b’ 1Sigma_u+ 12.854
b 1Pi_u 12.500

c’ 1Sigma_u+
c 1Pi_u
o 1Pi_u

<u>To Do:</u> Find out the dissociation energy limits of the N states

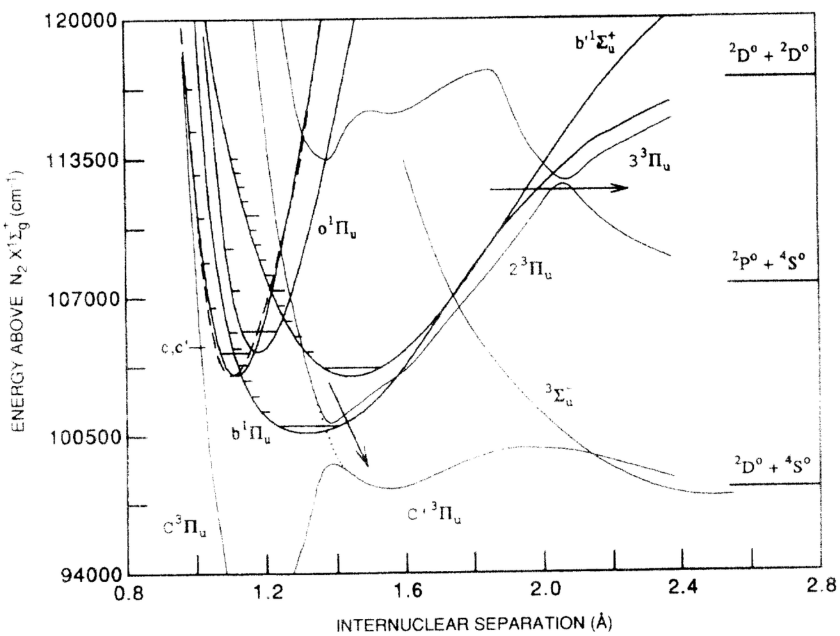


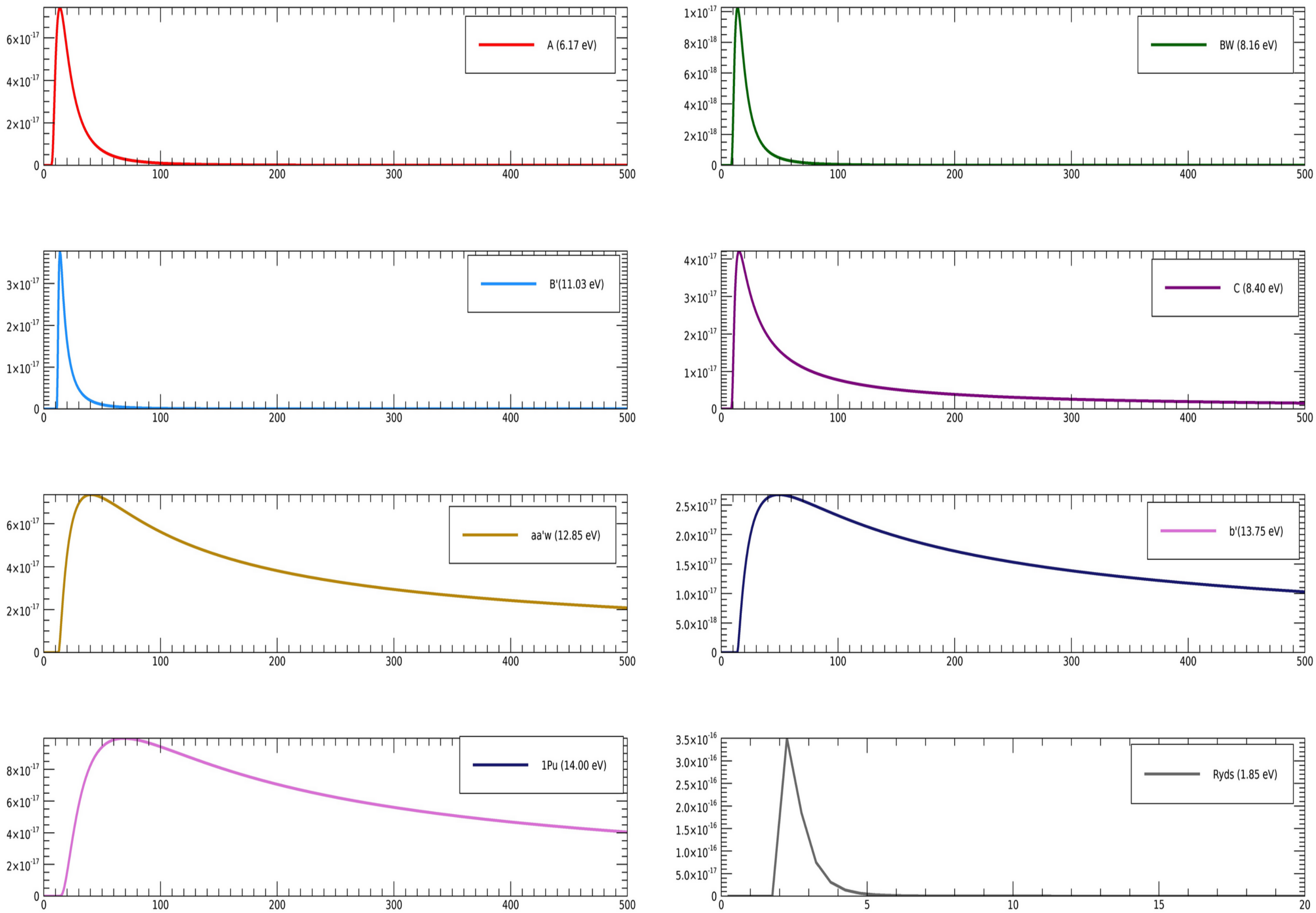
FIG. 1. Potential-energy diagram of excited single ungerade nitrogen states, together with candidate predissociating states. Arrows indicate dominant predissociation paths involving the $^3\Pi_u$ state.

II. <u>Current ones in the PE Model</u>

Has the following excitation states

A	6.17
BW	8.16
B’	11.03
C’	8.40
aa’w	12.85

1Pu 14.00
b’ 13.75
Ryds 1.85
vib 0.



Cross-section (cm^2) vs Energy(eV)

III. <u>Itikawa_2005-</u>

This paper has a compilation of cross-sections for different cross-sections as follows:

Total Cross-sections:

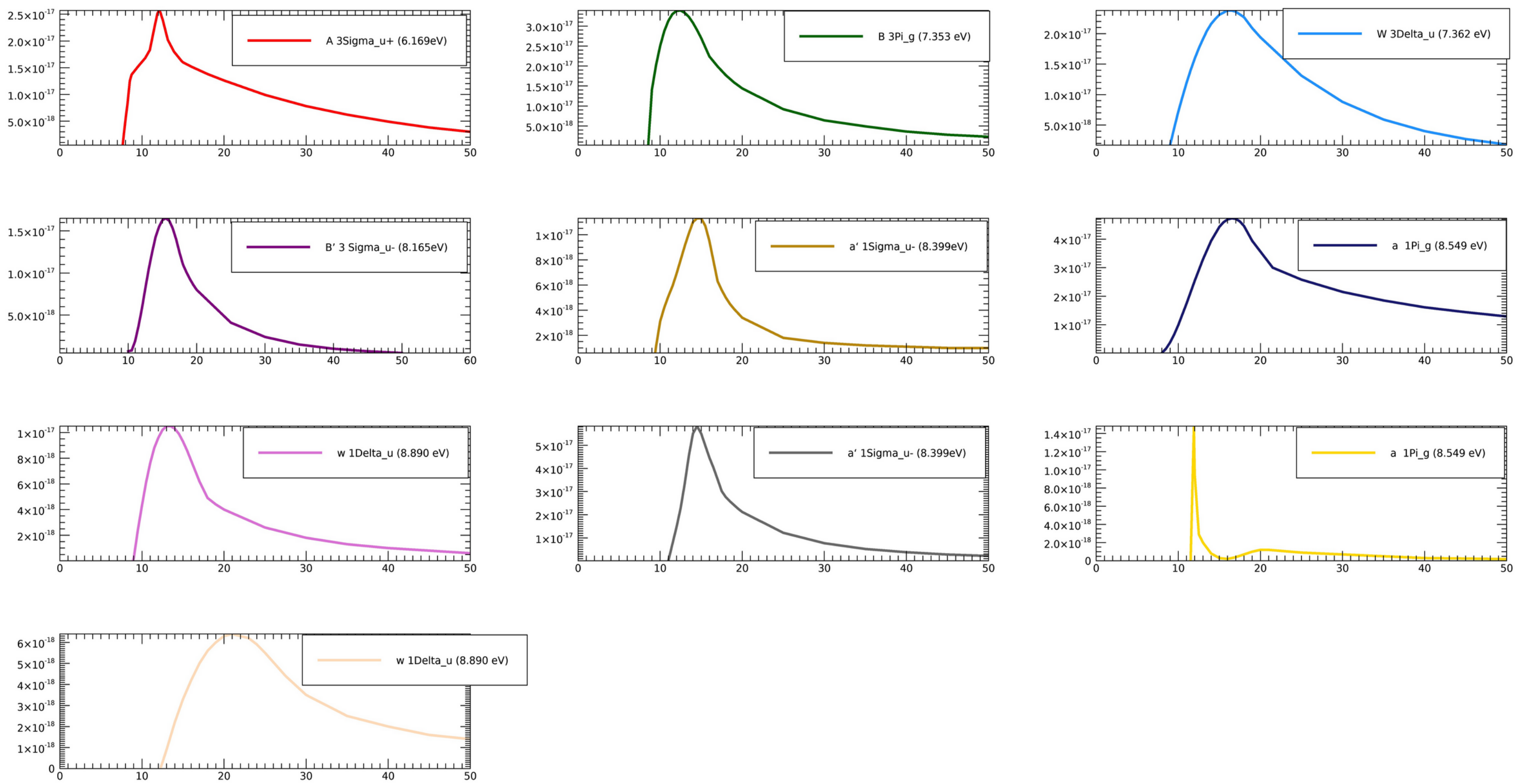
1. Elastic Scattering cross-sections
2. Momentum-transfer cross-sections
3. Rotational Cross-sections

4. Vibrational Cross-sections
5. Excitation of Electronic States
6. total dissociation cross-sec

These are the lower states less than 12.5 eV. There are table summaries for energy vs. cross-sections for the lower excited states which are plotted below.

Excitation of Electronic States

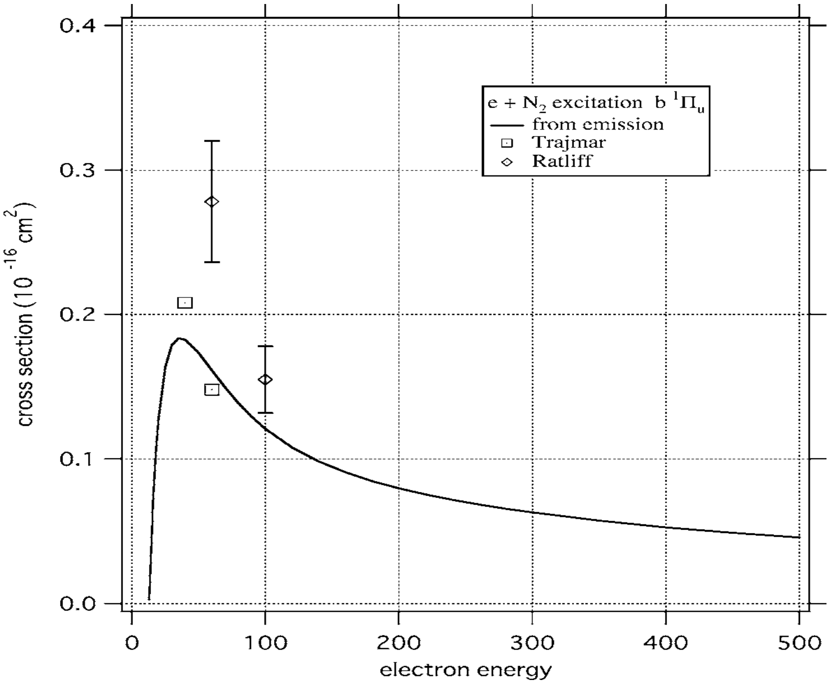
lower states	To (eV)
A 3Sigma_u+	6.169
B 3Pi_g	7.353
W 3Delta_u	7.362
B’ 3 Sigma_u-	8.165
a‘ 1Sigma_u-	8.399
a 1Pi_g	8.549
w 1Delta_u	8.890
C 3Pi_u	11.032
E 3Sigma_g+	11.875
a’’ 1Sigma_g+	12.255



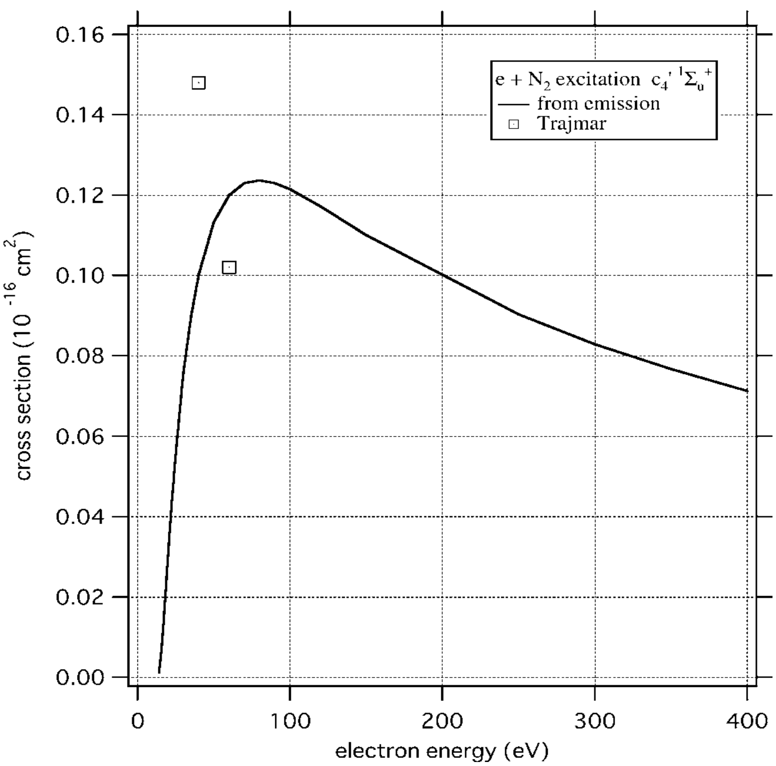
There are upper states which have threshold energies greater than 12.5 eV. The paper only has plots for these states.
upper states

b 1Pi_u 12.500

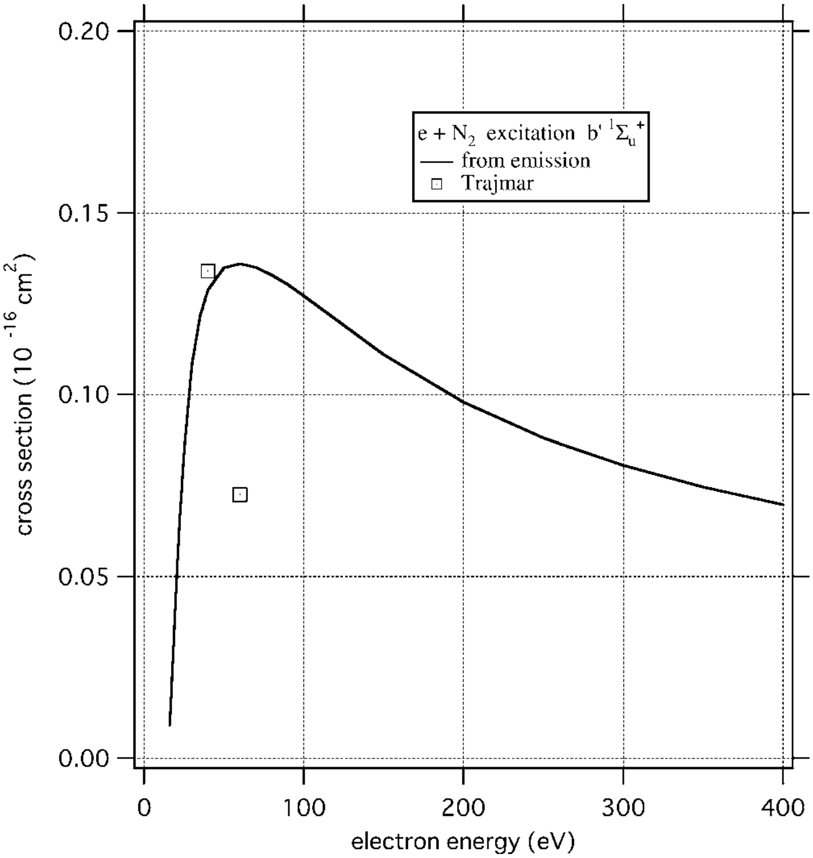
c’4 1Sigma_u+	12.935
b’ 1Sigma_u+	12.854



Emission Measure from: [68]G. K. James, J. M. Ajello, B. Franklin, and D. E. Shemansky, J. Phys. B23, 2055 (1990).



[70]J. M. Ajello, G. K. James, B. O. Franklin, and D. E. Shemansky, Phys.Rev. A 40, 3524 (1989).



[70]J. M. Ajello, G. K. James, B. O. Franklin, and D. E. Shemansky, Phys.Rev. A 40, 3524 (1989).

Other upper states :
F 3Pi_u
G 3Pi_u
c 1Pi_u
o 1Pi_u

<u>The b 1Pi_u state</u>

Relationship between cross-section and energy: (Shemansky 1985)

$$\sigma_{ij} E = \frac{\Omega_{ij}}{\omega_i}$$

$$where, \sigma_{ij} = cross - section$$

$$E = electron\, energy$$

$$\Omega_{ij} = collision\ strength\left(lower\ vibrational\ state\ i - higher\ state\ j\right)$$

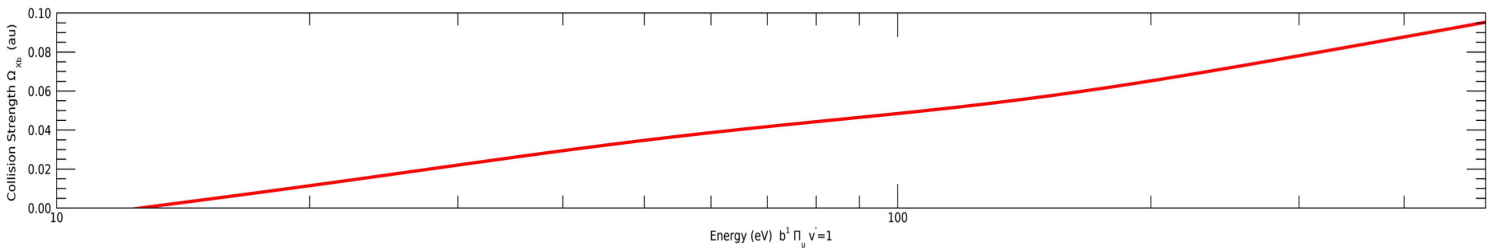
$$\omega_i = lower\ state\ degeneracy$$

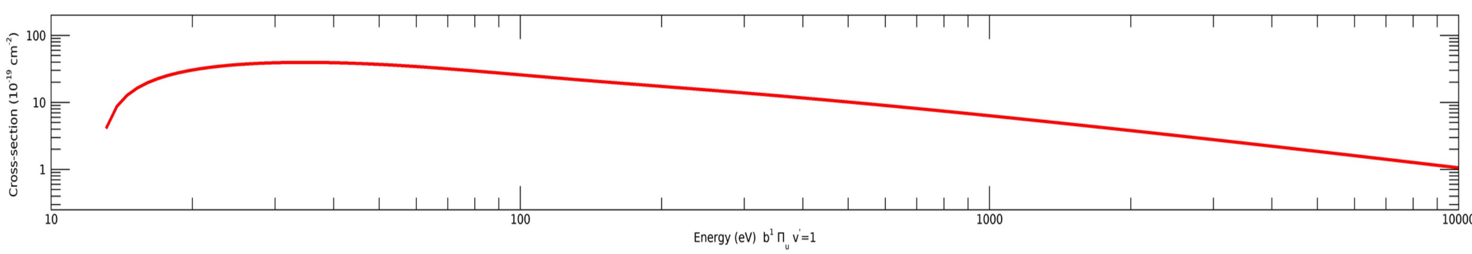
Ajello (1989) has the collision strength fitting function: I used this collision strength and the fitting constants from the James 1990 paper for the excitation cross-sections and the collision strengths plots given below:

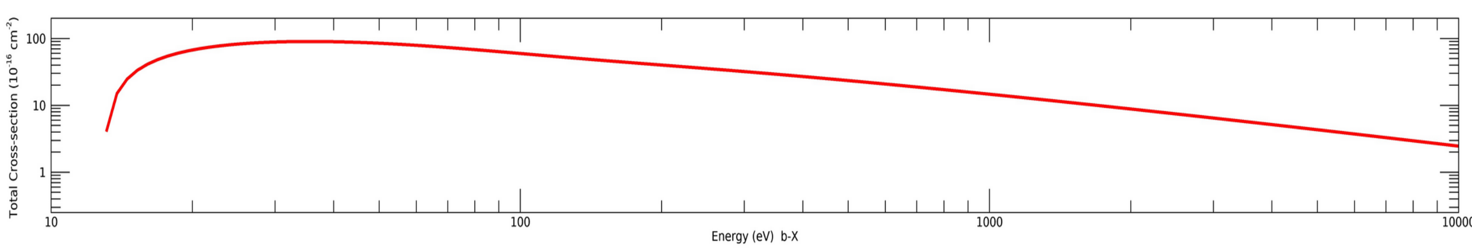
$$\Omega_{ij}=C_0\left(1-\frac{1}{X}\right)\left(\frac{1}{X}\right)+\sum_{n=1}^{4} C_n (X-1)\exp(-C_8 X)+\frac{C_6}{X}+C_7 \ln X \text{ where}$$

$$X=\frac{E}{E_{ij}}$$

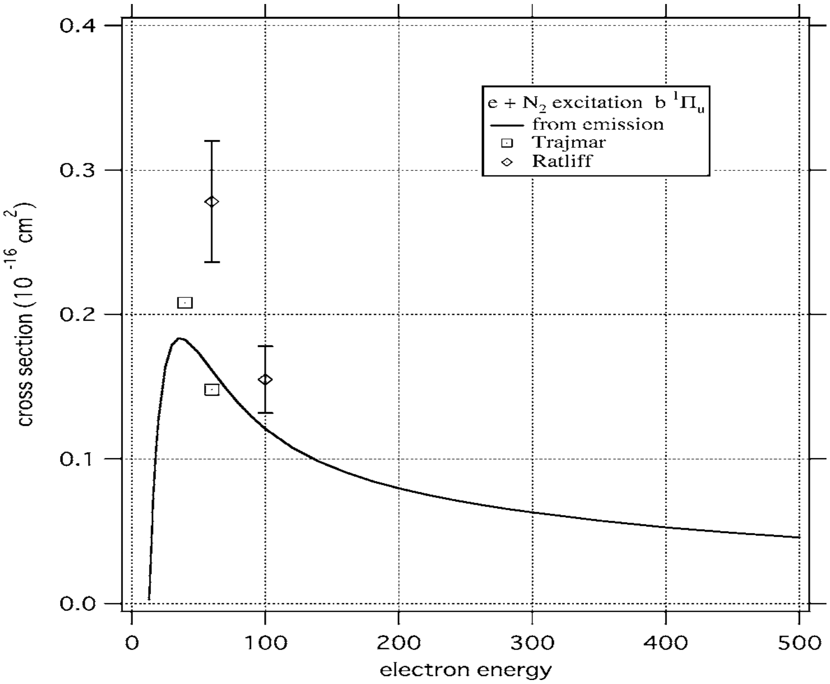
The collision strength is similar to the plot given in the paper (James 1990 figure 9). The excitation cross-section is ~10 times more than what is plotted in the paper. This maybe due to some unit conversion mistake or some normalization mistake that I am making, I am trying to understand the problem.
The paper lists the pre-dissociation, which is the ratio of the emission cross-section and the emission cross-section for different vibrational states of the b-X band. The b 1Pi_u state predissociates about 95% from this result.







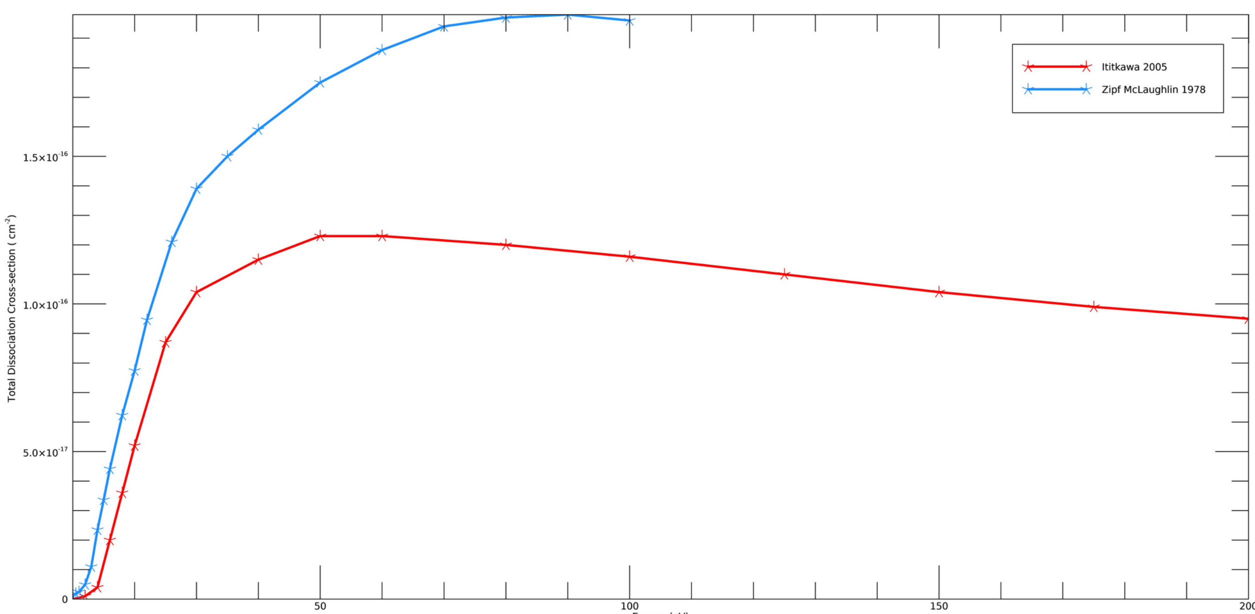
If we compare the excitation cross-sec plot in the third panel above to the one shown below taken from the total emission cross-sections from James et al 1990 paper, then there is a 100 times difference . I am still in the process of identifying the error.



Emission Measure from: [68]G. K. James, J. M. Ajello, B. Franklin, and D. E. Shemansky, J. Phys. B23, 2055 (1990).

If we can fit the emission and excitation cross-sections for all the higher energy states , then their ratios can give us the dissociation branching ratios

Also, I compared the Itikawa 2005 compilation of the N2 dissociation cross-sections to the Zip McLaughlin 1978 paper and the results are very different. The different states that are included in these two papers are different. Itikawa paper also has electron impact dissociative ionization states added in it.



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