

## Abstract

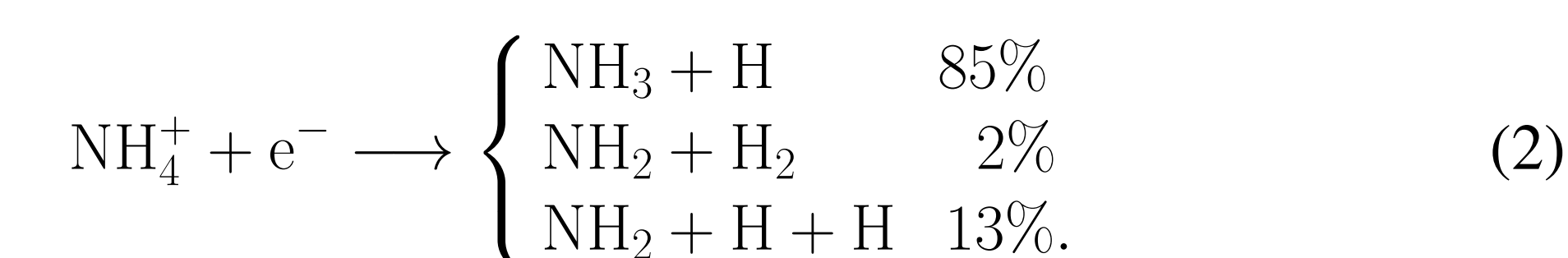
We apply a general theoretical model to study the dissociative recombination (DR) of the polyatomic ion  $\text{NH}_4^+$ . The high symmetry of the molecule, represented by the tetrahedral group, leads to complex vibronic couplings responsible for dissociative recombination. By applying multi-channel quantum defect theory and using symmetry considerations, we treat the doubly and triply degenerate modes and electronic states of  $\text{NH}_4^+$  and  $\text{NH}_4$  to calculate a theoretical cross section in good agreement with existing experimental data.

## 1 Introduction

Theoretical models to describe the dissociative recombination (DR) of polyatomic ions of more than two atoms have shown to be far from simple. The difficulty of the theoretical description of DR arises from the complexity of working in a multi-dimensional space. However, for highly symmetric closed shell molecular ions, which usually undergo DR at low energy mainly through an indirect mechanism, theoretical studies have shown that the presence of degenerate states is the main factor of the DR mechanism. Focusing on the key ingredients of the reaction, a simple model has already been developed and successfully applied on a number of polyatomic ions, such as  $\text{HCO}^+$  [1],  $\text{H}_3^+$  [2],  $\text{H}_3\text{O}^+$  or  $\text{CH}_3^+$  [3]. We adapt the model to a more complicated system like  $\text{NH}_4^+$  with tetrahedral symmetry. This ion plays an important role in the metabolism of animals, the atmosphere of planets and the nitrogen cycle in interstellar clouds. In the latter regions, it is primarily formed by the chain of reactions:



and is mainly destroyed by DR [4]:



The theoretical treatment of DR in  $\text{NH}_4^+$  involves new effects related to vibronic couplings in a molecule with triply and doubly degenerate modes and electronic states.

## 2 Theoretical Approach

We use the multi-channel quantum defect theory (MQDT) formalism and the vibrational frame transformation, to derive a DR cross section, averaged over resonances, for electronic capture in excited Rydberg states (autoionization and rotation of the system are neglected). The harmonic approximation is used to represent the vibrational states of the ion. We consider initial and final electronic states  $e$  and  $e'$  with irreducible representations  $\Gamma_e$  and  $\Gamma_{e'}$  of the  $T_d$  group. Assuming the ion initially in its ground vibrational state, the partial cross section for the capture of an incident electron in a (continuum) state  $e$  into another state  $e'$  (resonance), via the vibronic coupling involving the  $q_{i,\beta}$  vibrational mode with  $v_i'$  vibrational quanta of excitation is

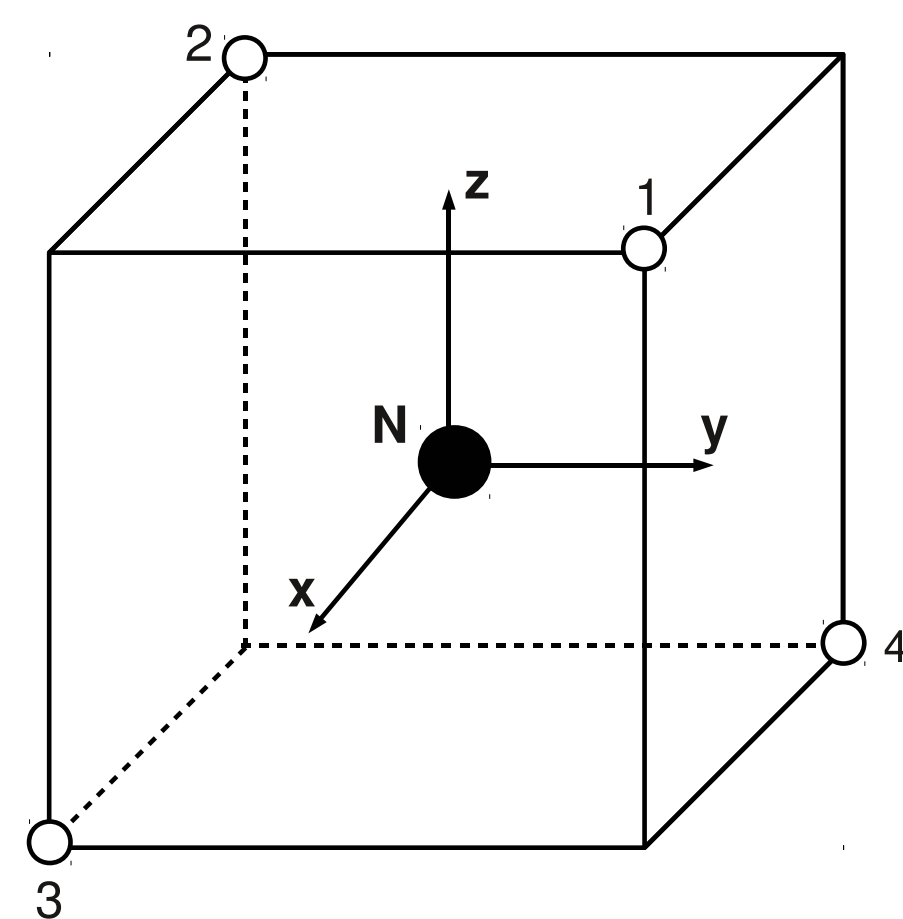
$$\sigma_{i,\beta}^{(e \rightarrow e')}(E) = \frac{\hbar^2 \pi^3}{m_e E} \left( \frac{\partial \mu_{e',e}}{\partial q_{i,\beta}} \right)_{\mathcal{Q}_e}^2 \theta(\hbar \omega_i - E) \delta_{v_i',1}. \quad (3)$$

The total cross section for all possible transitions is

$$\sigma^{(total)}(E) = \sum_i \sum_\beta \sum_e \sum_{e'} \sigma_{i,\beta}^{(e \rightarrow e')}(E). \quad (4)$$

## 3 Tetrahedral Symmetry

The quantum defect matrix is expressed as  $\hat{\mu} = \hat{\mu}^{(0)} + \hat{\mu}^{(1)}$  [3], where  $\hat{\mu}^{(0)}$  is a coordinate independent matrix and  $\hat{\mu}^{(1)}$  is a small quantum defect matrix such that  $\hat{\mu}^{(1)}(\mathcal{Q}_0) = 0$ . The matrix  $\hat{\mu}$  is totally symmetric under any transformation ( $E$ ,  $8C_3$ ,  $3C_2$ ,  $6S_4$  and  $6\sigma_d$ ) of the group  $T_d$  with irreducible representations  $A_1$ ,  $A_2$ ,  $E$ ,  $F_1$  and  $F_2$ .



### 3.1 Symmetry of the electronic states

We consider partial waves  $l = 0, 1$ , and  $2$  for the incident electron:

- The  $s$ -orbital has  $A_1$  irreducible representation.
- Denoting by  $C$  the rotation of angle  $2\pi/3$  around the axis passing through hydrogen 1, the real orbitals ( $p_x, p_y, p_z$ ) transform in cyclic permutation. We easily conclude that  $p$ -orbitals form a  $F_2$  irreducible representation.
- Considering the real  $d$ -orbitals and using equivalent arguments, we conclude that  $d_{xy}, d_{yz}, d_{zx}$  form a  $F_2$  irreducible representation and  $d_{z^2}, d_{x^2-y^2}$  form a doubly degenerate  $E$  irreducible representation. Thus,  $d$ -orbitals are decomposed as  $F_2 \oplus E$ .

### 3.2 Symmetry of the normal modes

Structure calculations were performed on  $\text{NH}_4^+$  to find its equilibrium position, vibrational frequencies and normal mode coordinates. We use a standard  $cc\text{-pvtz}$  basis with  $s$ -,  $p$ -, and  $d$ -orbitals. The calculated vibrational frequencies are in good agreement with the values reported in [5].

$\omega_i(\text{cm}^{-1})$	$\omega_i(\text{cm}^{-1})$	$\Gamma$	$q_i$
Present calculation	Martin <i>et al</i> [5]		
1491	1493	$F_2$	$(q_{1x}, q_{1y}, q_{1z})$
1743	1743	$E$	$(q_{2a}, q_{2b})$
3388	3395	$A_1$	$q_3$
3509	3516	$F_2$	$(q_{4x}, q_{4y}, q_{4z})$

### 3.3 Symmetry of the quantum defect matrix

The form of the elements of the quantum defect matrix  $\mu_{ij}(\mathcal{Q}) = \int \psi_i \mu(\mathcal{Q}) \psi_j dr$  between electronic states  $\psi_i$  and  $\psi_j$  can be found using symmetry considerations [6].

- In the basis of triply degenerate electronic states, transforming in cyclic permutation, the quantum defect matrix  $\hat{\mu}^{(1)}$  takes the form

$$\begin{pmatrix} \frac{1}{2}\kappa_e(q_a - \sqrt{3}q_b) & \kappa_f q_z & \kappa_f q_y \\ \kappa_f q_z & \frac{1}{2}\kappa_e(q_a + \sqrt{3}q_b) & \kappa_f q_x \\ \kappa_f q_y & \kappa_f q_x & -\kappa_e q_a \end{pmatrix}. \quad (5)$$

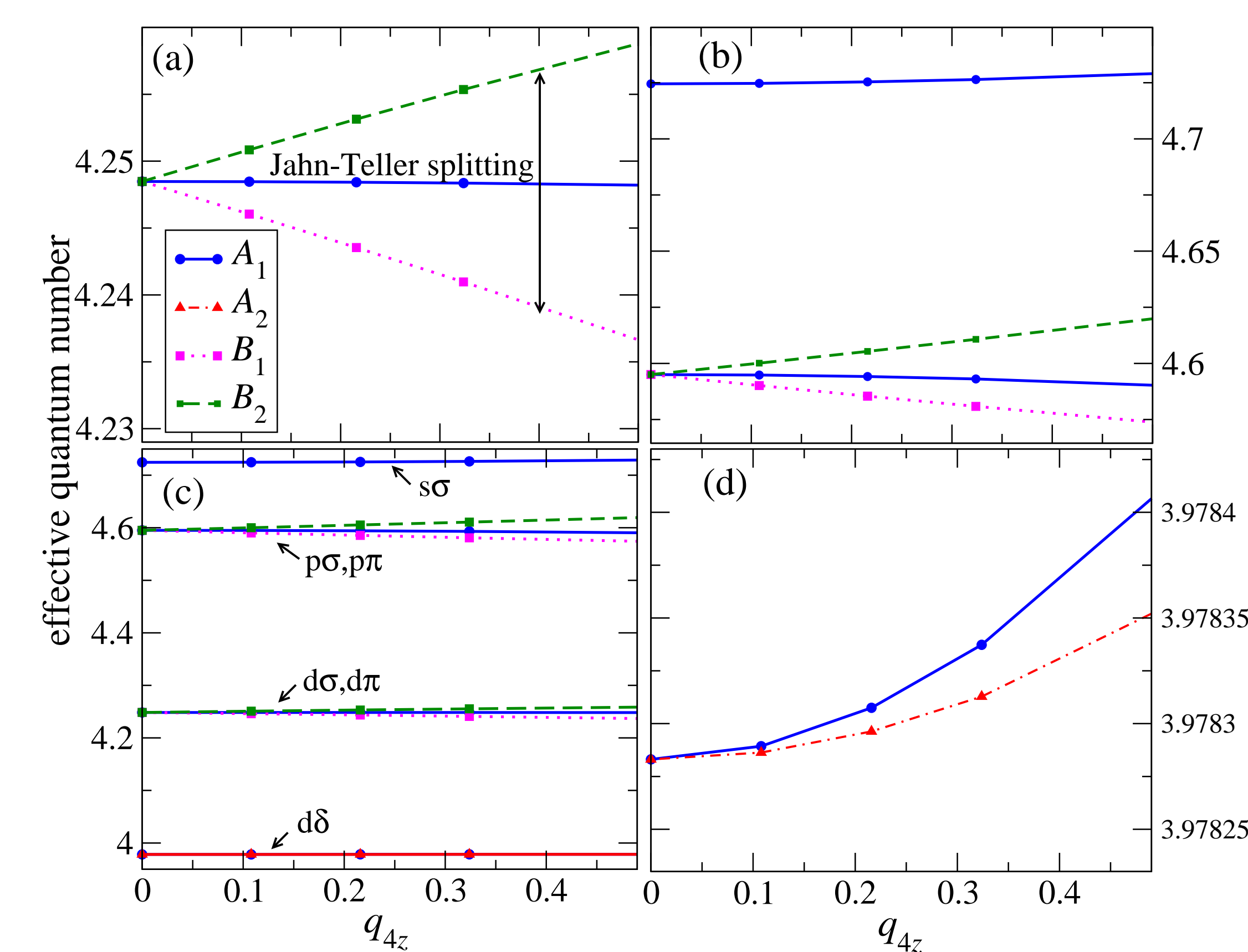
- In the basis of doubly degenerate electronic states, using complex coordinates  $q^\pm$  and electronic wave functions  $\psi^\pm = \psi_a \pm i\psi_b$  ( $C\psi^+ = \omega\psi^+$  and  $C\psi^- = \bar{\omega}\psi^-$ , with  $\omega = e^{2i\pi/3}$ ), the matrix  $\hat{\mu}^{(1)}(\mathcal{Q})$  takes the form

$$\begin{pmatrix} 0 & f_e q^+ \\ f_e q^- & 0 \end{pmatrix}. \quad (6)$$

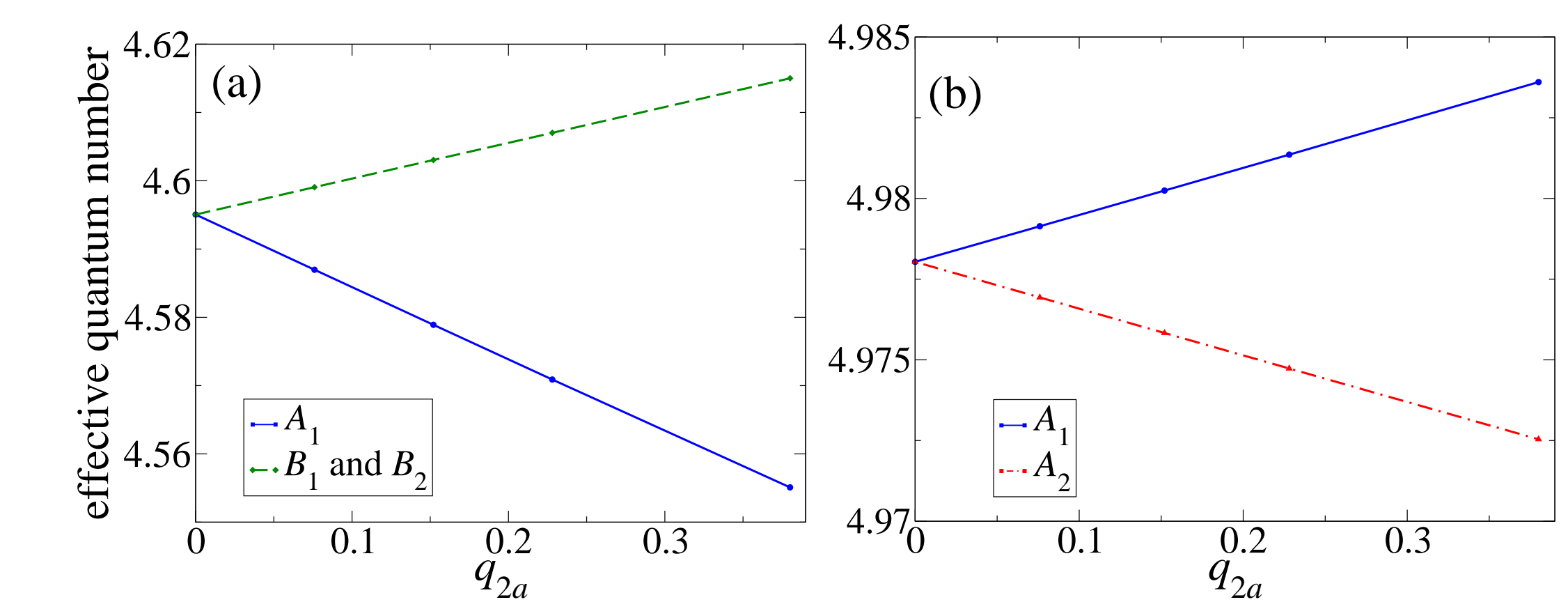
## 4 Rydberg states

We calculate Rydberg states of the neutral system  $\text{NH}_4$  until principal quantum number  $n = 5$ , by augmenting the initial basis with universal Rydberg  $s$ -,  $p$ -, and  $d$ -orbitals to obtain potential energy surfaces  $U(\mathcal{Q})$  of  $\text{NH}_4$ . The effective quantum numbers  $\nu(\mathcal{Q})$  are obtained from the Rydberg formula.

### 4.1 Distortion along a triply degenerate coordinate



### 4.2 Distortion along a doubly degenerate coordinate



## 5 Electronic Couplings

Couplings for degenerate states are found by fitting the Rydberg energies to the form (5) and (6). Couplings between two states  $\psi_a$  and  $\psi_b$  with different energies are also taken into account using a perturbative approach [7]:

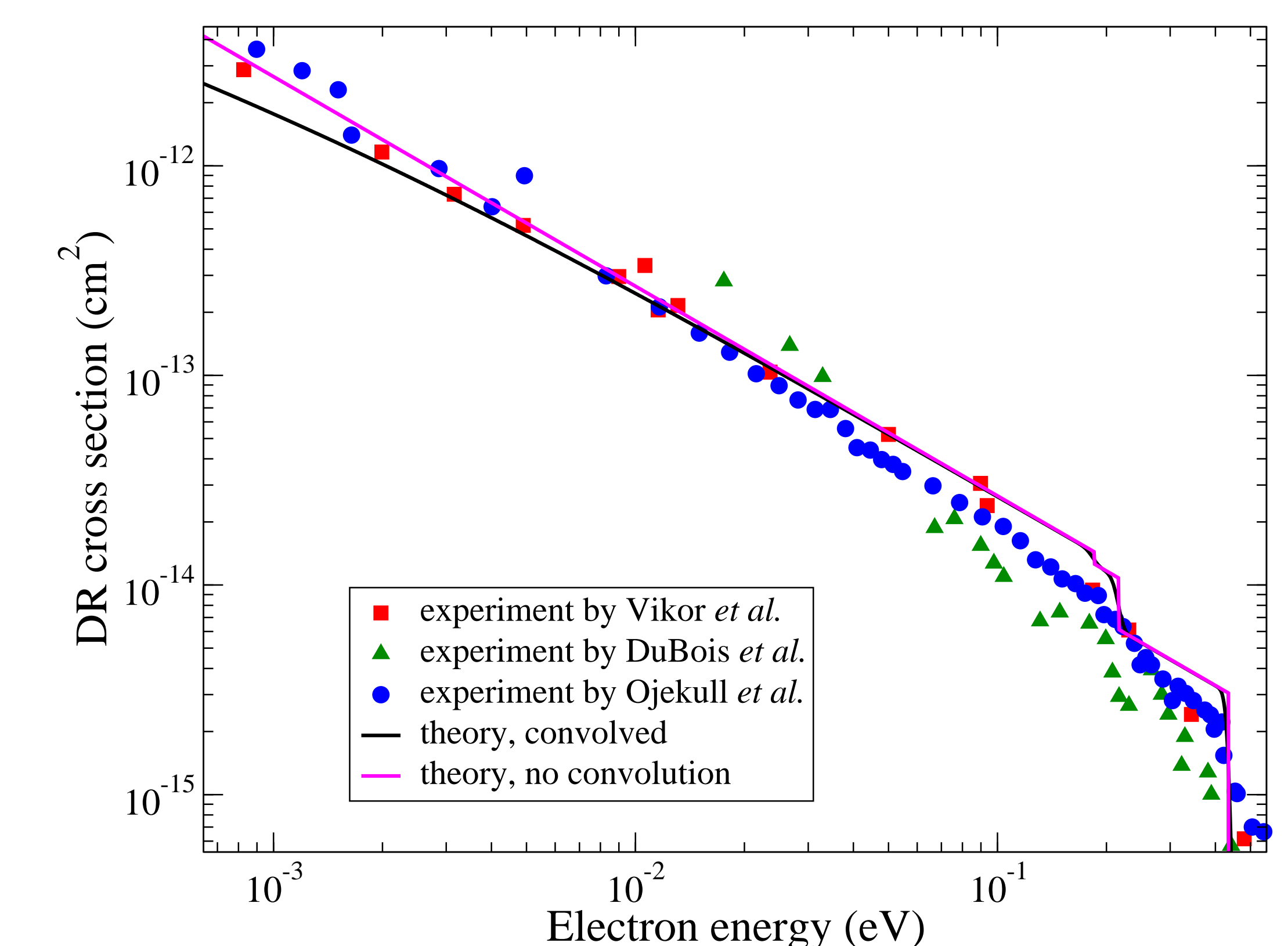
$$\mu_a = \mu_a^{(0)} + \frac{\hbar_a^2 q_z^2}{|\mu_a^{(0)} - \mu_z^{(0)}|}; \quad \mu_z = \mu_z^{(0)} - \frac{\hbar_a^2 q_z^2}{|\mu_a^{(0)} - \mu_z^{(0)}|}. \quad (7)$$

The values of the coupling between different electronic states, as well as the partial cross section for each mode (in  $10^{-16} \text{cm}^2 \times \text{eV}$ ), are given below

	$\kappa_f$	$\kappa_f$	$\hbar_a$	$\hbar_f$	$f_e$	$\kappa_e$	$\kappa_e$	$E\sigma$
$\nu$	$p \leftrightarrow p$	$d \leftrightarrow d$	$s \leftrightarrow p$	$p \leftrightarrow d$	$d \leftrightarrow d$	$p \leftrightarrow p$	$d \leftrightarrow d$	
4.595	4.248	4.725/4.595	4.595/4.248	4.978	4.595	4.248		
$q_1$	0.033	0.007	0.023	0.024	0.0	0.0	0.0	3.18
$q_2$	0.0	0.0	0.0	0.041	0.015	0.107	0.021	9.72
$q_4$	0.046	0.022	0.047	0.065	0.0	0.0	0.0	12.81

## 6 Results and Conclusions

In the figure, we give the theoretical cross section with and without a convolution over experimental energy spread reported in [4]. An overall good agreement is observed between the present theory and the experimental data. The theoretical cross section has three sharp drops at energies corresponding to the degenerate vibrational frequencies. The experimental cross-sections decrease also near these energies but the three sharp drops are not distinct, the most likely due to the limited resolution of the experiments.



In conclusion, we report, to our knowledge, the first DR study for a molecular ion with triply degenerate electronic states and normal modes. In addition, we stress that even for a complex molecule as  $\text{NH}_4^+$  with many degrees of freedom, this simple approach, which captures the critical physics of the DR process, provides excellent agreement with experimental data.

## Acknowledgements

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