Dissociative Recombination of CH^+

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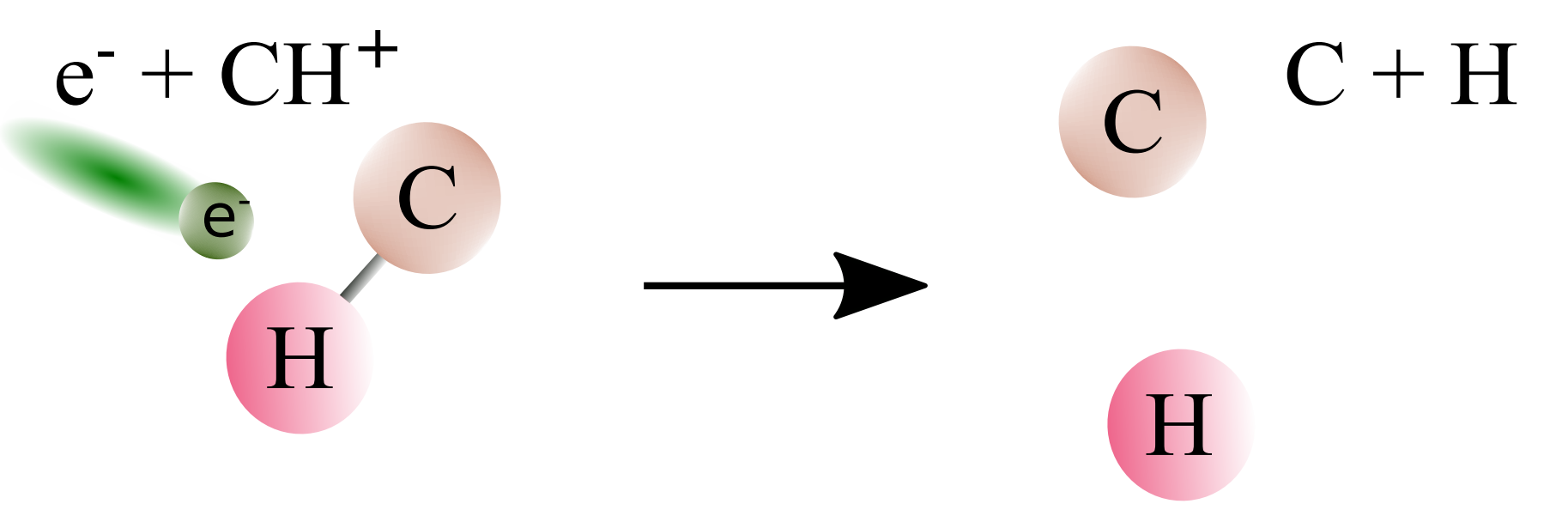
Motivation

Dissociative recombination (DR) is the main destruction mechanism of the CH^+ ion in the interstellar medium. CH^+ plays an important role in the formation of larger hydrocarbons.



The cross section for DR in CH+ was measured in a number of experiments and modelled theoretically using the Quantum Defect Theory (QDT) by the group of I. Schneider. Theory was able to explain the low-energy DR cross section.

The difficulty in theoretical treatment of DR in CH^+ is the presence of electronic resonances at low energies of e^--CH^+ scattering and a competition between direct and indirect mechanisms of DR in CH^+.

Here, we suggest a relatively general method to compute DR corss sections for the ions with low-energy electronic resonances. The method can also be applied to open-shell ions.

Theory

The presently accepted main dissociation pathway, at low energies, is thought to be the neutral $2^2\Pi$ dissociative state (see Fig. 1). At small values of the internuclear distance, R, it is of Rydberg character because it is created by the closed excitation channels of CH^+. Therefore, it can be represented by quantum defects associated with the excited electronic states $a^3\Pi$ and $A^1\Pi$ of the ion.

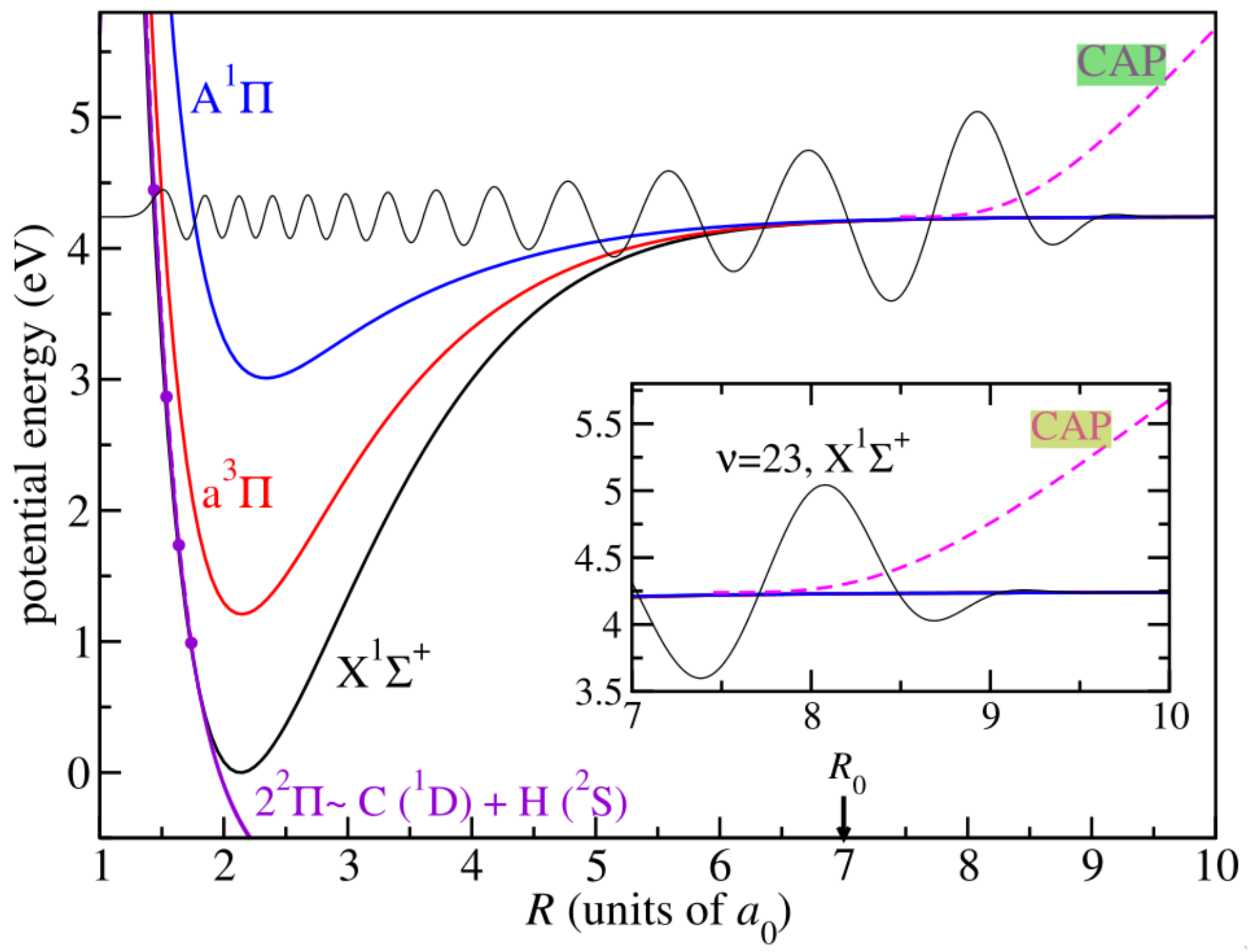


Fig. 1: The potential curves of the three lowest electronic states of CH^+ (black, red, blue) and the dissociative state (violet) are plotted, as well as one vibrational wavefunction (v=23) and the CAP (pink dashed line).

We perform electron scattering calculations using Quantemol at energies above the second excited state $A^1\Pi$ of the ion. At these energies, three electronic channels of the ion (show in Fig. 1) are open for ionization.

One can obtain the dissociative state by applying the closed-channel elimination procedure. Fig. 2 compares the resonances obtained for three values of R by the channel-elimination procedure and calculated directly by solving the electron-scattering problem as a function of the scattering energy.

However, we will perform the procedure only after the rovibrational frame transformation.

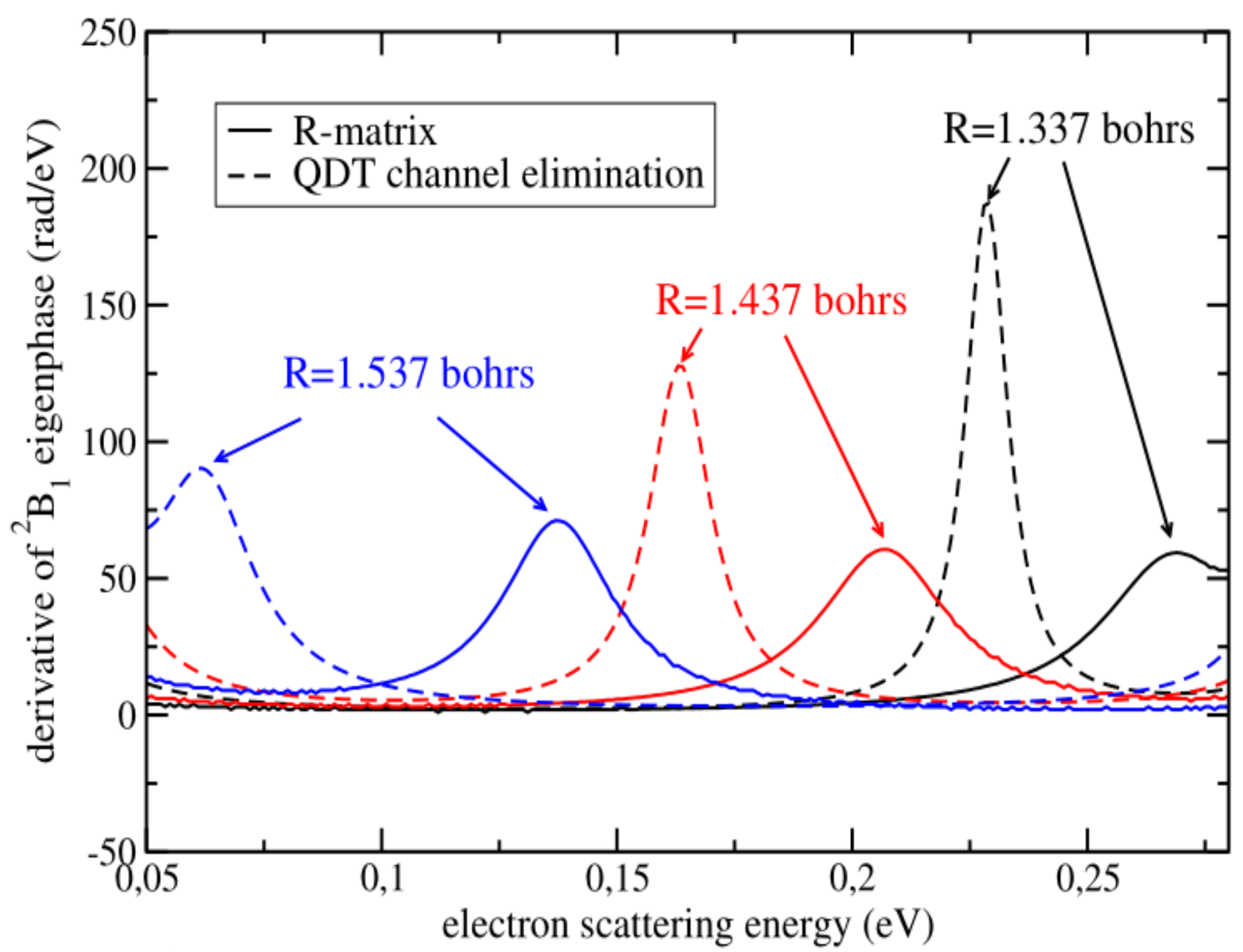


Fig. 2: The $2^2\Pi$ resonance evaluated for three geometries using (solid lines) the direct solution of the electron-scattering problem (Quantemol) and using (dashed lines) the closed-channel elimination procedure.

The procedure of rovibrational frame transformation, applied to the scattering (or reactance) matrix having three open electronic states of the ion, produces a matrix with no boundary conditions applied. The boundary conditions are applied by eliminating closed rovibronic channels.

In practice, we first calculate the reactance (K) matrix for several values R at energies above $A^1\Pi$ state of the ion.

Then, we obtain the matrix of phases (Δ-matrix) in the same basis as the K-matrix, (eigenvalues of the Δ-matrix are eigenphases) and extrapolate it over R (1.137-9.937 bohrs)

We diagonalize the extrapolated Δ-matrix and contsruct the electronic body-frame S-matrix

$$\Delta^{\text{ext}}(R) = U_{\text{ext}}^{-1}\ \delta^{\text{ext}}(R)\ U_{\text{ext}}$$
$$S(R) = U_{\text{ext}}^{-1}\ e^{2i\delta^{\text{ext}}(R)}\ U_{\text{ext}}$$

In this study, we neglect the rotational structure, but include vibration. To do so, we perform vibrational frame transformation on the S-matrix

$$S_{l'\lambda'v'i',\lambda vi} = \int dR\ \phi_{v'i'}(R)\ S_{l'\lambda'i',l\lambda i}(R)\ \phi_{vi}(R)$$

The wave functions ϕ_{vi} are the eigenstates of the vibrational Hamiltonian of the ion obtained placing a complex absorbing potential (CAP) at large distances (R>7 bohrs). In such calculations we obtain energies and wave functions of bound vibrational states and states of discretized continuum. The states of discretized continuum of the ion have large energies and, normally, are closed for ionization at low e-CH^+ scattering energies. However, they generate Rydberg states of the CH molecules that have a dissociative character. Therefore, the possibility of dissociation is accounted for in the scattering matrix after the vibrational frame transformation.

Due to the CAP, energies of discretized continuum states are complex.

$$E_{vi} = E_{vi}^{\Gamma} - i\frac{\Gamma}{2}$$

Next, we determine whether channels are energetically open (o) or closed(c) and partition our S-matrix

$$S \equiv \begin{pmatrix} S^{oo} & S^{oc} \\ S^{co} & S^{cc} \end{pmatrix}$$

We then obtain the physical S-matrix through channel elimination

$$S^{phys}\left(E_{\text{el}}\right) = S^{oo} - S^{oc}\left[S^{cc} - e^{-2i\beta(E_{\text{el}})}\right]^{-1} S^{co}$$
$$\beta\left(E_{\text{el}}\right) = \frac{\pi}{\sqrt{2\left(E_{vi} - E_{\text{el}}\right)}}\delta_{v'i',vi}$$

The complex eigenenergies in the exponent result in a subunitary S-matrix. Our assumption is that this unitary defect is responsible for the description of the DR mechanism.

The DR cross section for the initial channel (l, λ, v, i) is

$$\sigma_{l\lambda vi}(E_{\text{el}}) = \frac{\pi\hbar^2}{2m_e E_{\text{el}}}\times \left[1 - \sum_{l'\lambda'v'i'} S^{phys}_{l'\lambda'v'i',l\lambda vi}(E_{\text{el}})\ S^{\dagger phys}_{l'\lambda'v'i',l\lambda vi}(E_{\text{el}})\right]$$

The total DR cross section from the ground state for all partial waves of the incident electron is then

$$\sigma_{total}(E_{\text{el}}) = \sum_{l\lambda} \sigma_{l\lambda 00}(E_{\text{el}})$$

Results

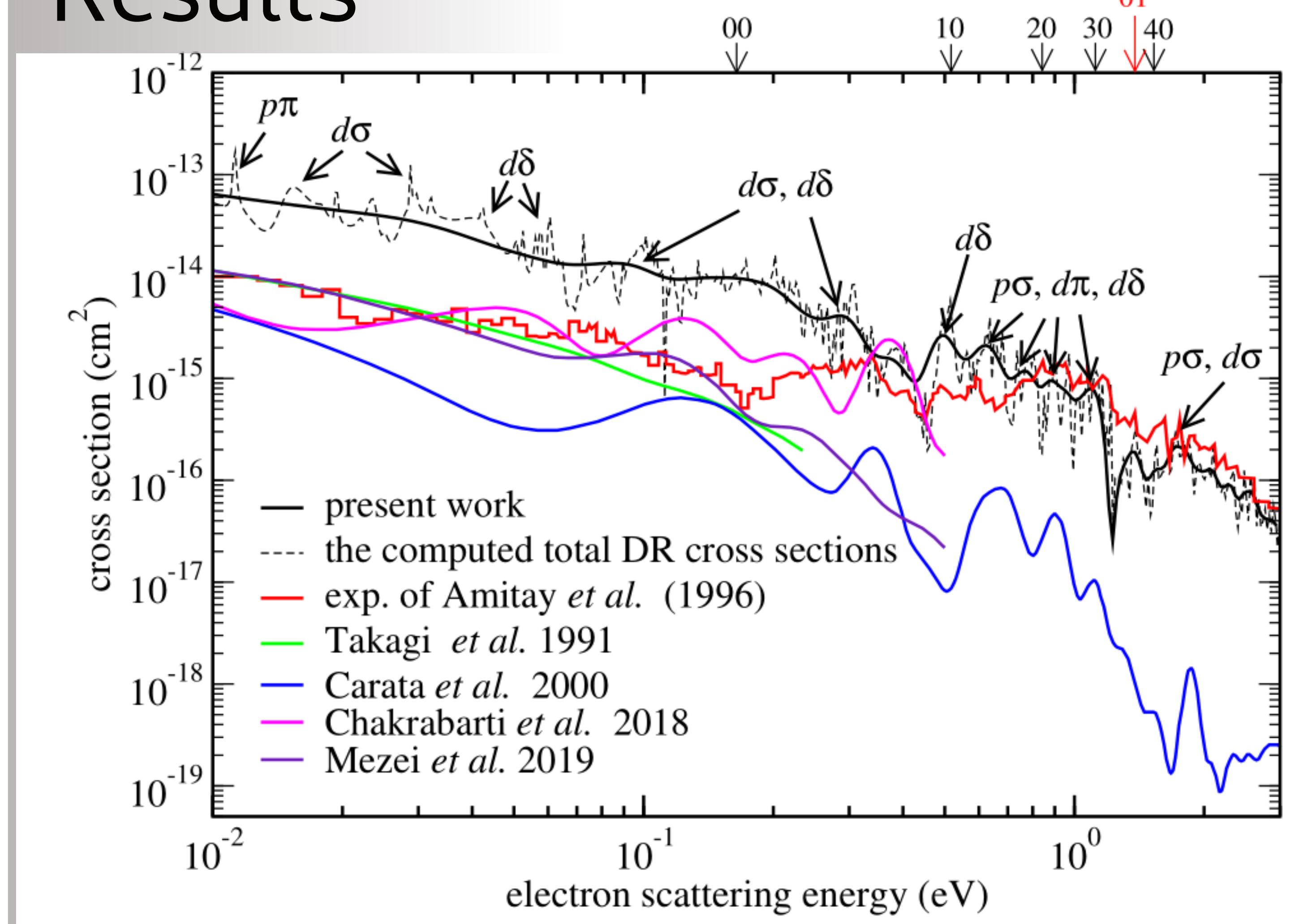


Fig. 3: The total DR cross sections of CH^+ from its ground vibronic state compared to previous theoretical calculations and experimental data

The arrows on the top axis indicate vibronic thresholds (vi), while arrows in the figure assign partial waves to resonances. Our results are close to the experimental values in shape and size above 0.03 eV, but are larger at lower energies. This may be due to the neglected rotational structure or the extrapolation approximation to avoid artificial matrix discontinuities. d-wave scattering had a surprisingly large contribution to our cross sections., although this was not considered in previous works.

Conclusion:

We have proposed a theoretical approach for modeling the DR in molecular ions where direct and direct mechanisms could be important. The approach seems to be well adapted for a large class of ions with low-lying electronic resonances, such as ions with open electronic shells.

In near future, we plan to implement the rotational structure.

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