

Ab initio CALCULATIONS FOR CO⁺ (FOR RADIATIVE ASSOCIATION IN SUPERNOVA 1987A)

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INTRODUCTION

Potential energy curves (PECs) and transition dipole-moment (TDM) functions for CO⁺ are calculated at the MS-CASPT2 level, following CASSCF calculations. Different basis sets and complete active spaces are employed, and different numbers of states are requested. The C_{2v} symmetry is employed.

The aim is to obtain reliable *ab initio* data for radiative association and radiative charge transfer calculations. The focus is on quartet states. The so-far published TDM functions for quartet states by other authors are sparse and do not cover all transitions of our interest (e.g. [1]).

MOTIVATION

We have dealt with formation of CO⁺ by radiative association in Supernova (SN) 1987A before [2,3]. Radiative association of two atoms is a collisional process during which a molecule is formed while emitting a photon. The desirable outcome of such a study is a rate coefficient that can serve as an input in astrochemical reaction networks.

FIG. 1 summarises how a supernova's environment can be studied. The highlighted part is our contribution to the whole picture: We do the dynamical calculations and if needed, also the *ab initio* calculations.

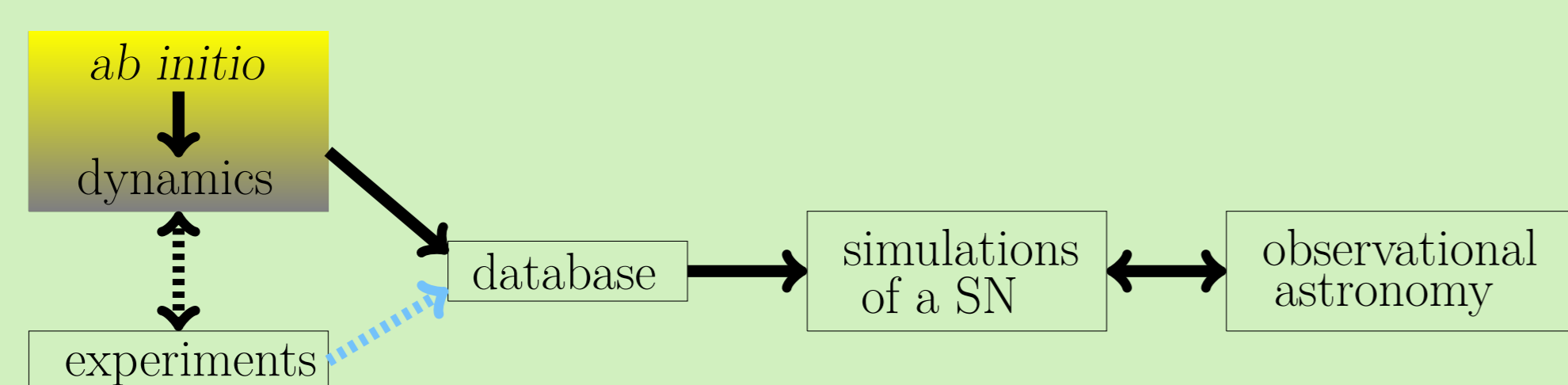


FIG. 1 A chronological scheme for a supernova's study: The dashed blue arrow indicates a lack of experiments for radiative processes. The dashed black double-tipped arrow indicates possible input data from experiments to theoretical studies and vice versa. The black double-tipped arrow indicates the close relation between the simulations and observational astronomy.

Rate coefficients are calculated from the corresponding cross section. To obtain the cross section, we need reliable PECs and TDM functions for all transitions that we expect to contribute significantly to the total radiative-association and/or radiative charge-transfer rate coefficient.

Previously, we calculated the PECs and TDM functions for doublet states of CO⁺ correlating to the lowest dissociation limit [2,3]. The total rate coefficient, restricted only to the lowest dissociation limit, exceeded our expectations. Further, we proposed a diabatic approximation for several processes [3]. The rate coefficients for such processes were sensitive to the choice of the representation. Therefore, we wish to study the influence of non-adiabatic couplings on the formation of CO⁺ properly (e.g. similarly as in NaCl [4]). For that, we need to calculate PECs and TDM functions for more electronic states and non-adiabatic couplings. FIG. 2 illustrates the calculated rate coefficients for individual transitions and the total rate coefficient, restricted to doublet states.

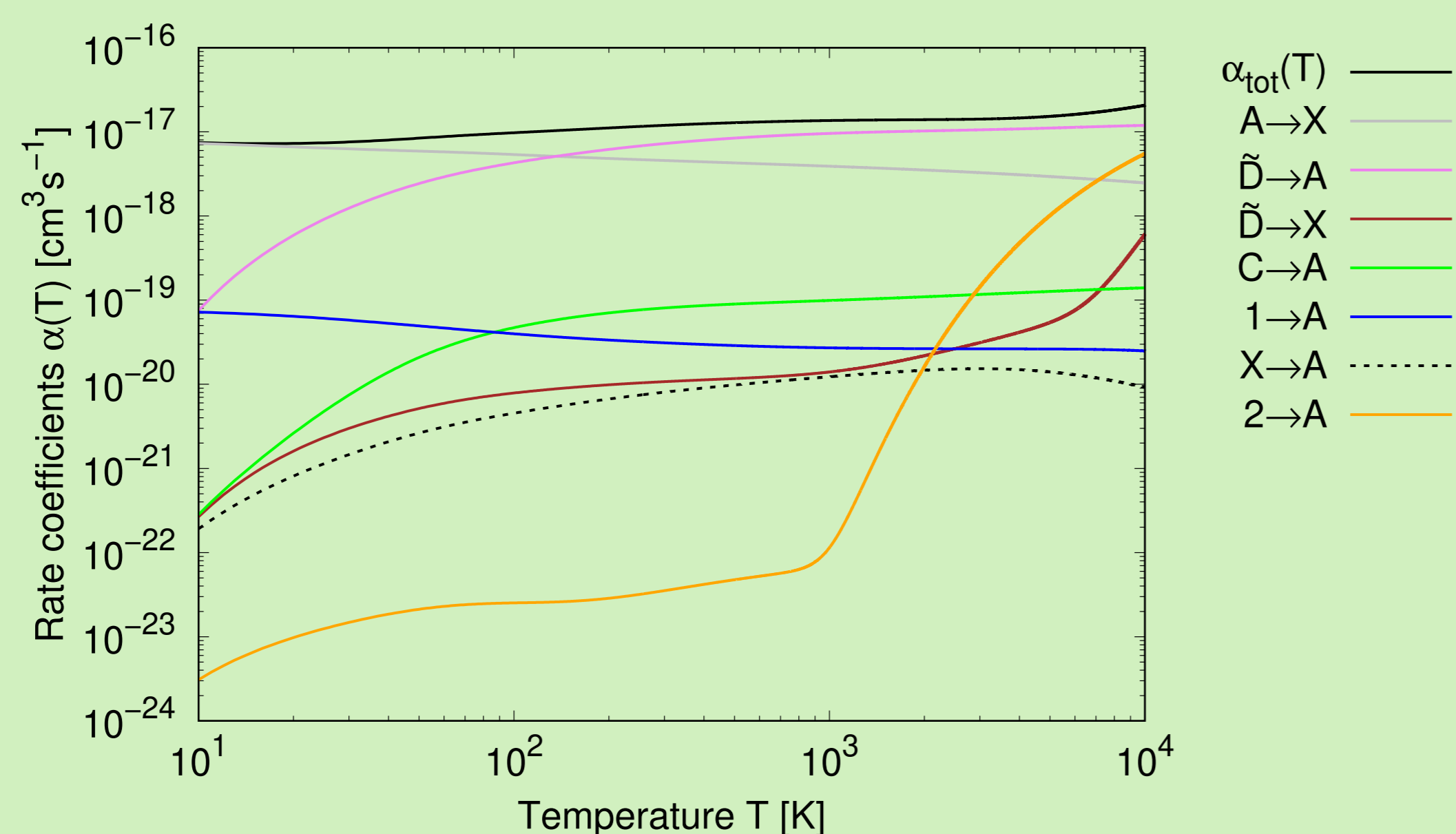


FIG. 2 The total rate coefficient for formation of CO⁺ by radiative association restricted to doublet states is illustrated and taken from ref. [2,3]. The tilde denotes that a diabatic approximation was applied.

REFERENCES

- [1] W. Xing, D. Shi, J. Zhang, J. Sun, Z. Zhu, *JQSRT* **210** (2018) 62–73.
- [2] M. Zámečníková, P. Soldán, M. Gustafsson, G. Nyman, *MNRAS* **489** (2019) 2954–2960.
- [3] M. Zámečníková, M. Gustafsson, G. Nyman, P. Soldán, *MNRAS* **492** (2020) 3794–3802.
- [4] M. Šimsová née Zámečníková, P. Soldán, M. Gustafsson, accepted to *A&A*.

METHODS

A series of calculations has been performed using the MS-CASPT2 method following the CASSCF calculations. We have tried different basis sets: aug-cc-pV5Z-DK, aug-cc-pV5Z, aug-cc-pVQZ-DK, aug-cc-pVQZ, cc-pV6Z, cc-pV5Z-DK, cc-pV5Z, cc-pVQZ-DK, cc-pVQZ. Within the C_{2v} symmetry, the A₁, B₁ and A₂ states were requested. Different complete active spaces were tried: CAS(9,8), CAS(9,12) and even CAS(9,14). For the MS-CASPT2 calculations, the imaginary shift was set to 0.1, 0.2 and 0.3. Different numbers of states were requested varying from 3 to 11 for A₁, from 3 to 60 for B₁, and from 3 to 11 for A₂. We are interested mostly in the states correlating to the lowest dissociation limits. TABLE I summarises the seven lowest dissociation limits, while we need states correlating at the maximum to the 7th limit, which is the fourth limit for quartet states.

The PECs were calculated for the internuclear distances from 0.3 a₀ to 10 a₀. For good candidates, the TDM functions calculations were performed.

TABLE I. The lowest dissociation limits for the CO⁺ system and their characteristics.

dissociation limit	states	symmetry	ΔE [cm ⁻¹]
1st C ⁺ (² P _u) + O(³ P _g)	Σ^+ , $2 \times \Sigma^-$, $2 \times \Pi$, Δ	doublet, quartet	0
2nd C ⁺ (² P _u) + O(¹ D _g)	$2 \times \Sigma^+$, Σ^- , $3 \times \Pi$, $2 \times \Delta$, Φ	doublet	15 867.9
3rd C(³ P _g) + O ⁺ (⁴ S _u)	Σ^+ , Π	doublet, quartet, sextet	19 016.7
4th C(¹ D _g) + O ⁺ (⁴ S _u)	Σ^- , Π , Δ	quartet	29 209.3
5th C ⁺ (² P _u) + O(¹ S _g)	Σ^+ , Π	doublet	33 792.6
6th C(¹ S _g) + O ⁺ (⁴ S _u)	Σ^-	quartet	40 664.7
7th C ⁺ (⁴ P _g) + O(³ P _g)	$2 \times \Sigma^+$, Σ^- , $2 \times \Pi$, Δ	doublet, quartet, sextet	43 003.3

We used two versions of OpenMolcas, concretely, OpenMolcas v18.09 and OpenMolcas v20.10 suits.

RESULTS

The smaller complete active space, CAS(9,8), gives better results for quartet states of CO⁺.

Basis sets cc-pV6Z and aug-cc-pVQZ-DK give the best results with the latter giving more reliable results for the A₁ states. Generally, the augmented basis sets seemed to describe better the dissociation limits (the number of states correlating to them and the qualitative shifts between the limits). The -DK basis sets seemed to find the minima more reliably.

FIG. 3 illustrates the preliminary MS-CASPT2 results in the aug-cc-pVQZ-DK basis set when 9, 29 and 5 states of A₁, B₁ and A₂ symmetry were requested. The OpenMolcas v20.10 suit was used for these curves. Requesting more states helped B₁ states to correlate to the correct dissociation limits. However, we could not get rid of numerical inconsistencies with dense grid around the avoided crossings between ⁴Π states.

The TDM functions were not satisfactory as they are very sensitive to any numerical inconsistencies in the PECs.

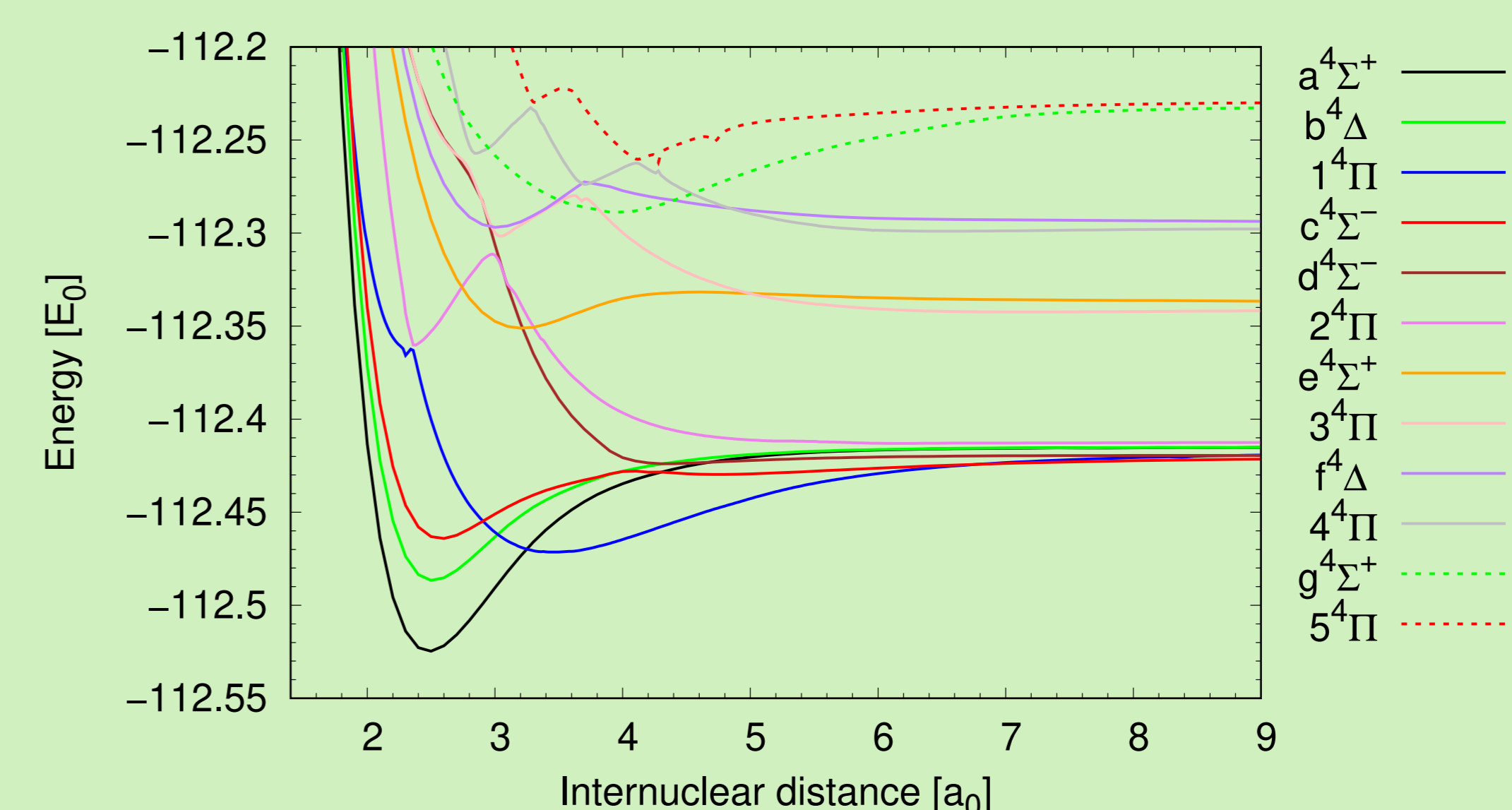


FIG. 3 The preliminary potential energy curves for quartet states of CO⁺ calculated by the MS-CASPT2 method are illustrated.

CONCLUSIONS

Preliminary results show that aug-cc-pVQZ-DK basis set gives the most stable results for the PECs for quartet states of CO⁺. The smaller complete active space, CAS(9,8), improved the results too. However, further calculations are necessary, especially for the B₂ states.

Later, the TDM functions will be calculated. It is also desirable to obtain the non-adiabatic couplings if possible.