CHAPTER SIX

Fock space coupled-cluster method for potential energy curves of KH and its cation

Magdalena Tomanek, Monika Musiał*, and Stanisław A. Kucharski
Institute of Chemistry, University of Silesia in Katowice, Katowice, Poland
*Corresponding author: e-mail address: monika.musial@us.edu.pl

Contents

Abstract

A multireference Fock space (FS) coupled-cluster (CC) method formulated in the (2,0) sector and an equation-of-motion CC method for a single electron attachment (equivalent to (1,0) sector of FS) are employed to investigate potential energy curves (PECs) and spectroscopic characteristics for the KH molecule and its molecular cation. The calculations were carried out at the single and double excitation levels (CCSDs) using the intermediate Hamiltonian formalism. For both approaches the adopted reference state is a doubly ionized molecular cation KH^{2+}. Such computational strategy has a concrete advantage for the calculations of PECs since the doubly positive ion dissociates into closed shell fragments; hence, the restricted Hartree-Fock (RHF) reference can be used over the whole range of interatomic distances. Results obtained (PECs and selected molecular constants) demonstrate that a first principles method can provide reliable theoretical data with an accuracy comparable or better than those generated by effective or model potentials containing adjustable empirical parameters.

1. Introduction

The studies of chemical reactions in cold and ultracold molecules are gaining popularity among both experimental and theoretical chemists.[1–6] The classes of compounds such as alkali hydrides and their ions are particularly useful in studies of collision phenomena, which allows the accurate determination of short- and long-range interatomic potentials.[7]

A common computational scheme used in the calculations of potential energy curves (PECs) for the alkali diatomics and alkali hydrides relies on the replacement of inner-shell electrons with the effective core potential (ECP).[8,9] In this manner the present computational task is reduced to the two-electron problem which can be solved, e.g., by using the configuration interaction (CI) method with inclusion of the singly (S) and doubly (D) excited configurations which in this case is the full CI (FCI) approach. For molecular cations, i.e., with one valence electron we solve the one-electron Schrödinger equation. The simple ECP model is subsequently improved by considering the inter-shell correlation effects represented by the core polarization potential (CPP).

In this work we focused on all-electron calculations looking for a rigorous *ab initio* scheme capable to describe the bond breaking process correctly. Although there exist a number of efficient and reliable quantum chemical methods (based on the coupled cluster (CC) or configuration interaction formalism) which can be used in the electronic structure calculations not all of them can be successfully applied in the study of alkali hydrides. This is connected with the fact that the construction of PECs describing bond dissociation is a particularly demanding task. This is so because the process of the homolytic dissociation of the single bond cannot be correctly described by the RHF (restricted Hartree-Fock) reference function. So this requires using the unrestricted HF scheme (UHF) with its well-known weaknesses of which the most painful are divergence problems in post-HF calculations.

Our proposition to solve this problem is an adoption of the different system to generate a Hartree-Fock reference function, i.e., instead of the AB molecule we may use the AB^{+2} ion[10–16] which dissociates into the closed shell fragments. The above approach can be used in the production of PECs for neutral molecule on condition that the applied quantum chemical method is capable to describe the system after attachment of two electrons to the reference, i.e., after recovering the original structure. The coupled cluster theory[17–19] offers so-called DEA (double electron attachment)

schemes.[10,20–23] We decided to use the multireference Fock space (FS) CC[23,24] scheme in the (2,0) sector[10] due to its rigorous size extensivity which is an important feature in PEC calculations. Same strategy was used for the molecular ion, KH^+, but in this case we used the EA-EOM-CC (electron attached equation–of–motion CC) method[25–29] ($\equiv$ FS-CC (1,0)) starting also from the KH^{+2} reference ($KH^{2+} \rightarrow KH^+$).

In previous work, focused on the Li_2 and LiNa molecules[11,12] using the above strategy, we were able to reach an excellent accuracy for spectroscopic constants. The KH molecule is a more demanding case because of the larger relativistic effects connected with the K atom. To account for this we have calculated the relativistic corrections to the spectroscopic constants. The scalar relativistic effects were included by combining the IOTC[30–34] (infinite-order two component) method and the FS-CCSD (2,0)[10] scheme. For this purpose, the local version of the FS-CCSD (2,0) module was interfaced to the GAMESS package. This was connected with the development of the necessary software.[12]

The key point is the intermediate Hamiltonian (IH) formulation[10,35,36] of FS-CC which offers an easy way to replace the iterative solution of the standard Bloch equation by the direct diagonalization of the properly constructed matrix ("dressed" $\overline{H}(\equiv e^{-T}He^{T})$ called IH matrix). Thanks to this we avoid all problems with the so-called intruder states which for years have blocked the wider application of this method. Moreover at the (1,0) level the IH strategy reduces the FS-CC methods to the EA-EOM-CC (EA—electron affinity).

2. Computational details

The calculations have been done using ACES II[37] and GAMESS[38] packages supplemented with the local version of the EA-EOM-CC[26] and IH–FS–CCSD (2,0) modules.[10,12] The spectroscopic constants have been determined using the LEVEL-8 program of Le Roy.[39] In all single and double electron attachment calculations the orbitals used are obtained by the RHF method for the KH^{+2} system in accordance with the overall computational strategy presented in the introduction. We used unANO-RCC+ basis set (228 basis functions), i.e. uncontracted ANO-RCC[40] basis set with two additional diffuse functions for the s shell, three additional diffuse functions for the p and d shells for potassium with exponents: 0.002 866, 0.001 143; 0.007 778, 0.003 111, 0.001 244; 0.107 098, 0.042 518, 0.016 879, respectively; three additional diffuse functions for the s shell, four additional

diffuse functions for the p shell, and one additional diffuse function for the d shell for hydrogen atom with exponents: 0.009 787, 0.003 425, 0.001 199; 0.034 589, 0.012 106, 0.004 237, 0.001 483; 0.011 642, respectively. The exponents were selected in the even tempered manner to ensure a proper ordering of atomic states of K and Li atoms. In order to estimate the role of relativistic corrections we have done PEC calculations with inclusion of scalar relativistic (SR) effects at the IOTC[30–34] level using the relativistic Sapporo-QZP+diffuse (SPKRAQZP) basis set[41] and the resulting corrections to the spectroscopic constants were obtained by comparing the relativistic values with those obtained in the standard nonrelativistic approach with the same basis set.[41] In all cases the spherical harmonic polarization functions were used with all electrons correlated. The active space for the IH-FS-CCSD (2,0) part has been set to 50, (i.e., 50 lowest virtual orbitals have been selected as active) for unANO-RCC+ basis set and 35 for Sapporo one. Total size of the basis set in Sapporo cases is equal to 144.

The results for the KH molecule are presented in Figs. 1–2 and Tables 1–2. The selected spectroscopic constants for the KH^+ molecular ion are collected in Table 3 and the PECs are presented in Fig. 3. The results obtained in this work include relativistic corrections and their values are given in parenthesis in the proper rows in Tables 2 and 3.
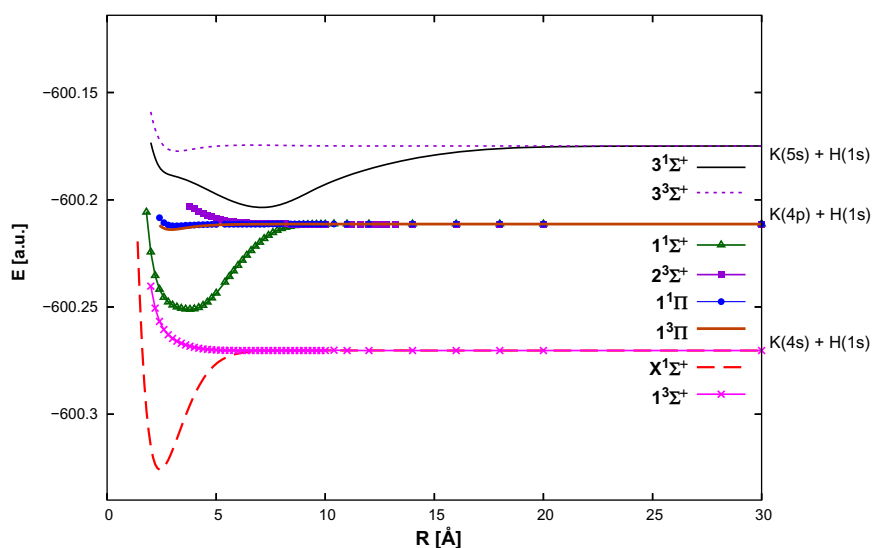

Fig. 1 Potential energy curves of the KH molecule with the IH-FS-CCSD (2,0)/unANO-RCC+ method for the three lowest lying dissociation limits.
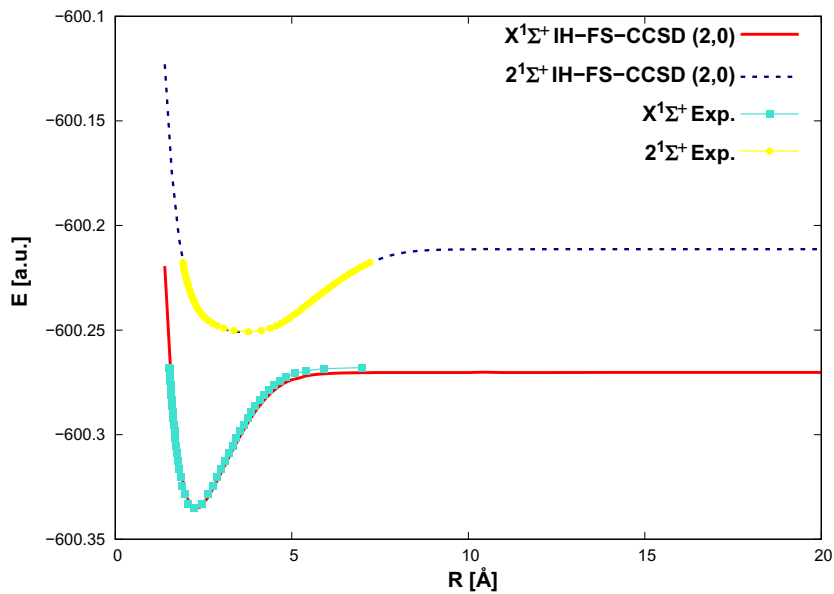
Fig. 2 Potential energy curves of the KH molecule with the IH-FS-CCSD (2,0)/unANO-RCC+ method for the $X^1\Sigma^+$ and $2^1\Sigma^+$ states—comparison with experiment.[42,43]

Table 1 Energy of the electronic states [a.u.] at the dissociation limit of the KH molecule compared to atomic energies in the unANO-RCC+ basis set.

Config. H	H energy	Config. K	K energy	H + K energy	KH energy
			EA-EOM-CCSD		**$R = \infty$ (200 Å)**
					IH-FS-CCSD (2,0)
1s	−0.499984	[Ar] 4s	−599.770285	−600.270269	−600.270269
1s	−0.499984	[Ar] 4p	−599.711347	−600.211331	−600.211331
1s	−0.499984	[Ar] 5s	−599.674970	−600.174954	−600.174954

3. Results and discussion

3.1 KH molecule

In Fig. 1 we show PEcs for nine electronic states of *KH* molecule obtained with the IH–FS–CCSD (2,0) method and converging to three dissociation limits: $K(4s) + H(1s)$ ($X^1\Sigma^+$, $1^3\Sigma^+$), $K(4p) + H(1s)$ ($2^1\Sigma^+$, $2^3\Sigma^+$, $1^1\Pi$, $1^3\Pi$), and $K(5s) + H(1s)$ ($3^1\Sigma^+$, $3^3\Sigma^+$).

Table 2 Spectroscopic constants for the KH molecule.

Sym.	R_e (Å)	D_e(cm^{-1})	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	T_e(cm^{-1})	Method
			$K(4s) + H(1s)$			
$X^1\Sigma^+$	2.242	14550	985	15	–	Exp.[42]
	2.273 (–0.003)	14282 (–34)	968(3)	14(0)	–	This work (IH–FS–CCSD (2,0))
	2.58	8025	–	–	–	Theor. (Pseudopot.)[44]
	2.24	14490	986	15	–	Theor. (Pseudopot. MCSCF)[45]
	2.27	12900	–	–	–	Theor. (Pseudopot.)[46]
	2.15	14990	979	–	–	Theor. (Pseudopot. CI)[47]
	2.265	15808	987	15	–	Theor. (DDCI)[49]
$1^3\Sigma^+$	6.945 (–0.009)	4(0)	–	–	14278 (–34)	This work (IH–FS–CCSD (2,0)
	unbound					Theor. (Pseudopot.)[44]
	6.35	22	–	–	–	Theor. (Pseudopot. MCSCF)[45]
	unbound					Theor. (Pseudopot.)[46]
	5.44	465	40	–	14524	Theor. (Pseudopot. CI)[47]
			$K(4p) + H(1s)$			
$2^1\Sigma^+$	3.68	9517	228	–	19060	Exp.[42,51]
	3.751 (–0.015)	8798(70)	235(3)	–4(0)	18554(31)	This work (IH–FS–CCSD (2,0)
	3.66	8860	226	–	19145	Theor. (Pseudopot. CI)[47]
	3.675	9598	255	–	19115	Theor. (DDCI)[49]
$2^3\Sigma^+$	unbound					This work (IH–FS–CCSD (2,0)
	unbound					Theor. (Pseudopot. CI)[47]

Table 2 Spectroscopic constants for the KH molecule.—cont'd

Sym.	R_e (Å)	D_e(cm^{-1})	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	T_e(cm^{-1})	Method
$1^1\Pi$	3.128 (−0.008)	189(4)	148 (3)	31(0)	27165(97)	This work (IH-FS-CCSD (2,0)
	3.14	293	155	–	27711	Theor. (Pseudopot. CI)[47]
$1^3\Pi$	2.845 (−0.005)	686(8)	307(−5)	35(−2)	26667(94)	This work (IH-FS-CCSD (2,0)
	2.78	855	317	–	27149	Theor. (Pseudopot. CI)[47]
			$K(5s) + H(1s)$			
$3^1\Sigma^+$	7.143 (−0.002)	6461 (−29)	171(0)	1(0)	28847 (101)	This work (IH-FS-CCSD (2,0)
$3^3\Sigma^+$	2.938 (−0.006)	757(8)	285(13)	36(2)	34551(64)	This work (IH-FS-CCSD (2,0)
	2.90	954	301.87	–	35063.54	Theor. (Pseudopot. CI)[47]

Table 3 Spectroscopic constants for the KH^+ molecular ion.

Sym.	R_e (Å)	D_e(cm^{-1})	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	T_e(cm^{-1})	Method
			$K^+ + H(1s)$			
$X^2\Sigma^+$	2.992 (−0.007)	366(6)	219(1)	34(0)		This work (EA-EOM-CCSD)
	3.17	452	202	–	–	Theor. (Model pot. approach)[53]
	2.92	384	372	–	–	Theor. (MRCISD)[52]
			$K(4s) + H^+$			
$2^2\Sigma^+$	4.676 (−0.007)	5114 (−58)	321(−1)	4(0)	70002 (−74)	This work (EA-EOM-CCSD)
	4.66	5267	323	–	70420	Theor. (Model pot. approach)[53]
	4.54	5329	312	–	69786	Theor. (MRCISD)[52]

Continued

Table 3 Spectroscopic constants for the KH^+ molecular ion.—cont'd

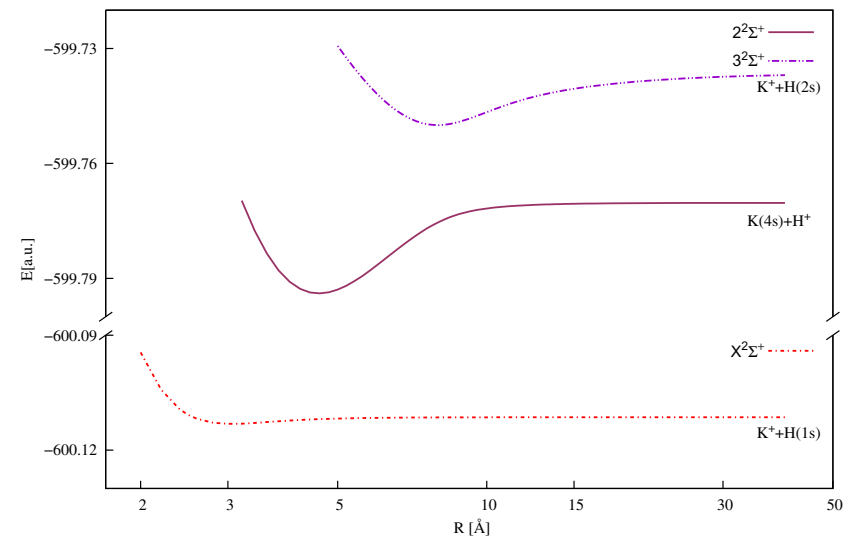| Sym.	R_e (Å)	D_e(cm^{-1})	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	T_e(cm^{-1})	Method
			$K^+ + H(2s)$			
$3^2\Sigma^+$	7.923 (0.028)	3010 (48)	154(2)	2(0)	79659 (−41)	This work (EA–EOM–CCSD)
	8.20	1976	145	−	79857	Theor. (Model pot. approach)[53]
	7.94	3154	150	−	79531	Theor. (MRCISD)[52]

Fig. 3 Potential energy curves of the KH^+ molecular ion with the EA-EOM-CCSD/unANO-RCC+ method for the ground and two excited states ($X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$).

In Table 1 we compare total energies of electronic states the KH molecule at infinite interatomic distance with the sum of energies for the K and H atoms. This comparison is crucial in the current calculations since for the size-extensive methods (which is the case for the FS-CC) the energies of the molecular electronic states should converge to the sum of respective atomic values at infinite distance and we observe a full coincidence of these numbers.

A majority of studied states are evidently bound (see Figs. 1 and 2 and Table 2) although for some of them, $1^3\Sigma^+$ and $1^1\Pi$, the potential well is very

shallow. For the $2^3\Sigma^+$ we observe around 10 Å a plateau rather than a well hence we treat this state as unbound. We are able to compare our theoretical PECs with the experimental ones in two cases – $X^1\Sigma^+$ and $2^1\Sigma^+$.[42,43] As we can see in Fig. 2 the coincidence between theoretical and experimental curves is excellent.

As mentioned in the introduction the theoretical studies of the electronic structure of alkali diatomics and alkali hydrides are dominated by the effective potential approach. This is true also for the KH example since most of the theoretical results quoted in Table 2 are of the ECP origin. The question is whether the rigorous first principles method can compete with the approaches where many parameters are empirically optimized to match desired results.

The values for the $X^1\Sigma^+$ state obtained in this work compare quite well with experiment: the equilibrium bond length is off by 0.03 Å, harmonic frequency by 17 cm^{-1} and dissociation energy by 268 cm^{-1}. Out of four pseudopotential–based works[44–47] the most reliable theoretical results are provided by Stevens et al.[45] They were obtained by a combination of the MCSCF wave function for valence electrons and the empirical core potential with several parameters adjusted to fit observed atomic spectra. A different type of pseudopotential, known as nonempirical or *ab initio* pseudopotential, was introduced by Barthelat and Durand.[48] On that basis Ross et al.[47] have carried out calculations for fifteen states of KH molecule. The D_e and ω_e values remain in good agreement with experiment (off by 440 and 6 cm^{-1}, respectively) while the optimum bond length R_e is too short by ca. 0.1 Å. The other two pseudopotential approaches[44,46] substantially underestimate the D_e value. In Table 2 we quote also the results of the strict *ab initio* approach based on the DDCI (Difference Dedicated CI).[49] These calculations reproduce quite well the R_e and ω_e constants (off by 0.023 Å and 2 cm^{-1}, respectively) giving at the same time a bit too large D_e value (by more than 1300 cm^{-1}).

For the $1^3\Sigma^+$ state the experimental data are not available. Out of four theoretical reports[44–47] two predict a repulsive potential[44,46] while the other two[45,46]—a shallow potential well. Stwalley et al.[50] in the review paper devoted to the spectroscopy and structure of alkali hydrides recommend for the D_e the value 22 cm^{-1} which is slightly larger than our 4 cm^{-1}. The adiabatic excitation energy is reported only in Ref. 47 and it agrees quite well with the value obtained in the current work.

A comparison with experiment can also be made for the excited singlet state. Results obtained in this work reproduce the D_e value with deviation of

ca. 700 cm^{-1} (0.09 eV) and T$_e$ with an error of 506 cm^{-1}. The theoretical values reported in Refs. 47 and 49 are close to the experimental values for all molecular quantities except for ω_e.

The molecular constants for the remaining states studied in this work can be compared only with the results of Ross et al.[47] We observe that they fit each other quite well with the differences in D$_e$ values less than 200 cm^{-1} and T$_e$ values ca. 500 cm^{-1}. Similar close coincidence can be seen in the case of R$_e$ and ω_e. The fact that the numbers quoted in Table 2 for the states $^1\Pi$ and $^3\Pi$ as well as $3^1\Sigma^+$ and $3^3\Sigma^+$ obtained in our rigorous *ab initio* method agree quite well with those obtained with entirely different approach suggests that—in the absence of experimental values—they can be treated as a source of reliable molecular data.

It should be also mentioned that the relativistic corrections (values quoted in parenthesis) are moderate in the case of R$_e$ (below 0.01 Å) and ω_e. For both energy parameters, D$_e$ and T$_e$, they are nonnegligible amounting for some states to 100 cm^{-1}.

3.2 KH$^+$ ion

Potential energy curves which are presented in Fig. 3 were obtained with the EA-EOM-CCSD method using the unANO-RCC+ basis set for the three lowest lying states correlating to the following dissociation limits: $K^+ + H(1s)$ ($X^2\Sigma^+$), $K(4s) + H^+$ ($2^2\Sigma^+$), $K^+ + H(2s)$ ($3^2\Sigma^+$). All states are bound (see Fig. 3 and Table 3).

Experimental molecular constants are not available so we are able to compare our data only with other theoretical results. Two relatively recent papers were devoted to the studies of alkali-hydride cations: one by Magnier[52] and the other by Yan et al.[53] The first one uses the model potential approach which reduces the many-electron problem to the solution of the Schrödinger equation for one electron moving in the effective potential. This approach uses a number of adjusted parameters thereby the theoretical values reproduce experimental data quite well for the molecules for which the latter exist. The second work reports the results based on the multireference CISD method with an essential modification that the K and L shell electrons were replaced by relativistic effective core potentials with fully correlated treatment of the remaining nine electrons (valence and highest inner shell). In most cases both approaches provide consistent results and the data obtained in the current approach fit in reasonably well.

The ground-state molecular constants (equilibrium bond length R_e, harmonic frequency ω_e, depth of the potential well D_e) obtained in all studies are close to each other. The current values of R_e and ω_e stay in between the values reported in other theoretical papers while the D_e value is off by 18 cm^{-1}[152] or 86 cm^{-1}.[53]

For the first excited state $2^2\Sigma^+$ the equilibrium position R_e and vibrational constant ω_e are very close to those in Ref. 53 (4.66 vs 4.676 Å) and the D_e value is lower by 150 cm^{-1} (less than 0.02 eV). The excitation energy value computed in the current work falls nearly in the middle of the distance separating these values in the literature.

The results computed in the current *ab initio* work for next excited state $3^2\Sigma^+$ stay very close to the outcome of model potential calculations. The difference in equilibrium bond length is below 0.02 Å, in harmonic frequency – below 5 cm^{-1} and in both energetic parameters (D_e and T_e) below 0.02 eV (ca. 130 cm^{-1}). The MRCISD results indicate larger bond length (by ca 0.3 Å) and substantial lowering of the D_e value – by 1000 cm^{-1}.

4. Conclusions

An adequate description of single bond breaking with rigorous *ab initio* method is not a trivial task in particular when the closed shell structure (in the vicinity of equilibrium geometry) dissociates into open shell fragments. In our approach this problem is circumvented by adopting as the reference a doubly ionized molecule which retains a closed-shell feature both at equilibrium and at large interatomic distances. By using the FS-MRCCSD scheme, formulated in the (2,0) sector, we are able to get smooth PECs for the whole range of interatomic distances.

The data reported demonstrate that the rigorous *ab initio* calculations carried out for all electrons in the system can provide reliable set of spectroscopic data for the alkali hydrides. In particular the relativistic corrections are revealed in the contraction of K-H bond in all electronic states and result in better agreement with experiment. Similarly nonnegligible relativistic contributions were obtained for the dissociation and excitation energies: e.g., in all but one state the T_e increases its value by ca. 100 wavenumbers.

Acknowledgments

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