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Interatomic potentials of the C-He system. Application to fine structure excitation of C (^3P_J) in collisions with He

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Abstract. Fine structure excitation cross-sections are calculated for C I ground state atoms by collisions with He in a close coupling quantal treatment after the relevant potential curves have been determined. The corresponding rates and cooling functions are then determined for temperatures relevant to interstellar clouds.

Key words: collisions – interstellar matter – C I

1. Introduction

The direct emission of the magnetic dipole transitions at 609.135 and 340.415 μm of neutral carbon which has been observed in various interstellar clouds (e.g. Jaffe et al. 1985; Keene et al. 1985) follows the collisional excitation of the fine structure levels of the ground ^3P state. Studies to date of the excitation of the C I fine structure lines have been performed for neutral atomic H impact (Launay & Roueff 1977), electrons (Johnson et al. 1987) and protons (Roueff & Le Bourlot 1990). We consider here the role of He atoms for populating the fine structure levels. He atoms represent indeed 10% of the total density in astrophysical environments. Moreover, it can give a reasonable estimate, after reduced mass effects have been taken into account, of the collisional excitation by H_2 molecules which are likely to be dominant in molecular clouds. We present in the second section the calculations of the relevant potential curves. In Sect. 3, we summarize the close coupling quantal theory of fine structure excitation and discuss the results obtained for the cross sections and rate coefficients.

2. Interatomic potential curves

Though calculations of potential energy surfaces of van der Waals diatomic molecules do not seem far different from another diatomic from a conceptual point of view, it remains a challenge for quantum chemists because involved well depths are typically of about hundred wavenumbers or less. The energies involved in the formation process are just one or two orders of magnitude above the precision generally required in ab-initio calculations. Particular care must then be brought in all steps of the calculation. In this paper, we present the first determination of the $^3\Pi$ and $^3\Sigma^-$ potential surfaces of C-He which intervene in the collision between C($2p^2\,^3P$) and He ($1s^2\,^1S$), following a method described in Lavendy et al. (1987). The atomic basis set for the C atom consists of the (12*s*, 7*p*) basis of Van Duijneveld (1971) contracted to (7*s*, 4*p*); it has been increased by two diffuse *s* (0.1, 0.05), one *p* (0.03) and two *d* functions (1.25, 0.3), in close analogy with values chosen by Staemmler & Jaquet (1985) referred as SJ in the following, in their calculation of the O-He potential curves. For He, we use the 7*s* basis set of Huzinaga (1965) contracted to (4*s*) increased by one diffuse *s*(0.059), four *p*(1.20, 0.4, 0.13, 0.06) and one *d* function (0.25) as was done by Miller et al. (1990) in their HeN_2^+ potential surface calculations. These diffuse and polarisation functions play a very important role in van der Waals calculations since they allow a much better description of dispersion and polarisation effects. The total energies are (in atomic units or in Hartrees): He(^1S): −2.896823 (C I) and C(^3P): −37.759178 (C I).

The properties that are most important for the van der Waals interaction are the polarisabilities of the subsystems C and He. As an indication of the quality of our basis set, we have computed the static dipole polarisabilities in calculating the energy of a system formed by the atom under study and a charge located at $R=20$ au. At the C I level, we found $\alpha(C)=8.30$ au compared to 11.88 au (Miller & Bederson 1977), and $\alpha(He)=1.377$ au compared to the experimental value 1.383 au.

The interaction energy can be decomposed into two main contributions: the intra-valence shell correlation on the one hand and polarisation and dispersion energy on the other hand. To calculate the intra-valence shell correlation, we started from the SCF orbitals respectively of the $^3\Pi$ and the $^3\Sigma^-$ state, and completed this set of orbitals by localized valence virtual orbitals: for the C atom, we take the weakly occupied orbitals resulting from the MCSCF calculation of the C(^3P) ground state (one *s*, and one *p*). We add orbitals located on concentrated *d*(1.25) function; for He, we use the natural orbitals (two *s*, one *p*) resulting from a full C I calculation of the He(^1S) state. All these orbitals are suitably orthogonalized. Single and double C I calculations give the main part of the correlation energies as well as the angular correlation and part of the dispersion energy. The C I space is then extended by monoexcitations from the ground state into specific diffuse orbitals to account for the polarization effects and simultaneous monoexcitations on each fragment to give the remaining part of the dispersion energy. These diffuse

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orbitals are located mainly on the diffuse atomic part of the basis set. We select one s, one p and one d orbital for the C atom and one p orbital for He, which are orthogonalized to the set of valence orbitals previously defined. About 900 configurations are considered in the C I matrix. All calculations have been done with the Hondo program (Dupuis et al. 1980). The interaction energy is defined as the difference, for each geometry between the energy of the supermolecule and the sum of the energies of the two fragments. However, due to the basis set superposition error (BSSE), the individual energies are lower than their values at infinite separation. We have calculated this BSSE at the SCF level using the counterpoise method of Boys & Bernardi (1970) and find a very small contribution (less than 2 μH at $R=5.0$ AU). The SCF-BSSE value is a measure of the quality of the atomic basis set. Our value indicates that each fragment is well represented by its own set of atomic orbitals. At the C I level, the BSSE can only occur in the valence orbitals because our treatment of the dispersion involves only monoexcitations on one center and nothing on the ghost system. The valence C I-BSSE value obtained is equal to 30 μH at $R=5.0$ which is small compared to the uncorrected interaction energy (265 μH for $^3\Sigma^-$ and 2157 μH for $^3\Pi$). Two reasons explain why the BSSE is so small, while it is currently admitted that it should be of the same order of magnitude as the interaction energy itself. First, we use quite localized orbitals, then we allow only monoexcitations on each fragment in the C I dispersion contribution. Results of the calculations are given in Table 1 and potential curves are drawn in Fig. 1.

We notice that the $^3\Sigma^-$ potential is less repulsive and deeper than the $^3\Pi$ potential. Their minima are respectively: $E_{\min}=-61.32$ μH at $R=6.31$ au and $E_{\min}=-13.53$ μH at $R=8.90$ au. This is just the inverse situation of the O-He interactions which can easily be explained from simple physical arguments: In C-He, the p_z orbital is monooccupied in the $^3\Pi$ state and empty in the $^3\Sigma^-$ state; hence the $^3\Pi$ potential is more repulsive than the $^3\Sigma^-$ potential at all internuclear separations. In O-He, the p_z orbital is doubly occupied in the $^3\Sigma^-$ state and only monooccupied in the $^3\Pi$ state: the $^3\Sigma^-$ potential is then more repulsive than the $^3\Pi$ potential. In order to estimate the precision obtained in our calculations, we have applied the method described above to the O-He interaction and compare our results and those given in (SJ) who use a CEPA (coupled electron-pair approximation) method in Table 2. We obtain a good agreement between the two methods although our potential curves show a tendency to be slightly more repulsive than those of SJ. We extend these potential curves by the long range C_6/R^6 dispersion term which we estimate from the formula given by SJ:

$$C_6^{AB}=(C_6^{AA}C_6^{BB})^{1/2}$$

where A and B refer respectively to C and He and C_6 is the van der Waals coefficient. Burke & Robb (1975) have given the values of the dispersion C_6 coefficient for two interacting carbon atoms as well as for two He atoms.

From their values we infer: $C_6(^3\Sigma^-)=-7.18$ au and $C_6(^3\Pi)=-6.975$ au for C-He interaction. The corresponding analytical expressions are then taken from $R=9$ AU for $V^3\Sigma^-$ (the numerical and analytical values are there almost identical) and from $R=12$ au for $V^3\Pi$.

3. Collision calculations and results

The quantal treatment of fine structure excitation due to collisions with neutral atoms has been the object of an extensive literature and will not be recalled in this paper. We simply mention a general review paper (Roueff 1990) where the basic theory is given. We have solved the relevant second-order differential equations by using the de Vogelaere algorithm (1955). The equations were integrated out to $R=30$ au which was sufficient to insure convergence of the inelastic cross sections which depend on the differences between the $^3\Sigma^-$ and $^3\Pi$ potential energy curves. The fine structure excitation cross sections obtained are given in Table 3 as a function of the incident kinetic energy on the $j=0$ level of C.

Monteiro & Flower (1987) have recently recalled a first order selection rule for the 0-1 fine structure transition in ^3P state atoms, such as O and C, induced by a structureless perturber such as He. They showed moreover that this selection rule is indeed well fullfilled in the case of O-He collisions where the $j=2$ state

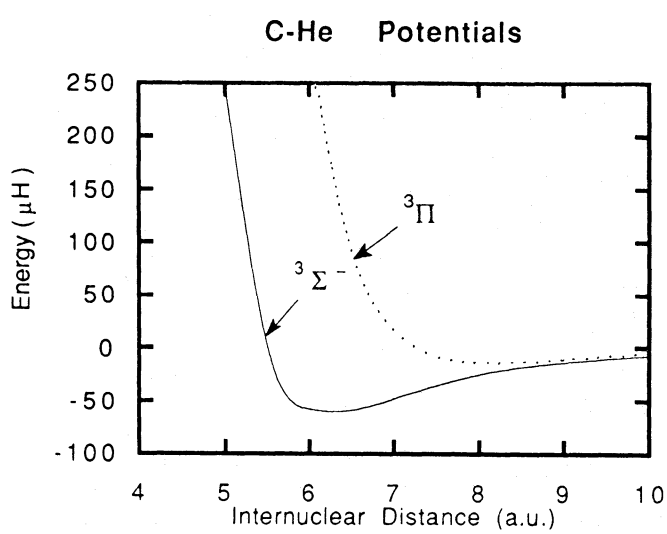

Fig. 1. Potential curves of the C-He system

Table 1. C-He interaction potentials

R (au)	SCF results[a]		C I results[a]	
	$^3\Pi$	$^3\Sigma^-$	$^3\Pi$	$^3\Sigma^-$
2.0			323 995	97559
3.0			71 922	21608
4.0			13 165	3297
5.0	2476	517	2157	247
5.5	1010	170	830	0
6.0	407	48	299	−58
6.5	167	13	93	−59
7.0	64	1	17	−48
8.0	9	−2	−13	−25
8.5	3	−1	−13	−18
9.0	1	0	−10	−13
30.0	0	0	0	0

[a] All quantities are expressed in μH: 1H = 1 au = 27.2 eV

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Table 2. O-He interaction potentials

R (au)	$^3\Pi$				$^3\Sigma^-$			
	CEPA method[a]		Present work		CEPA method[a]		Present work	
	SCF	C I	SCF	C I	SCF	C I	SCF	C I
5.0	439	64.9	439	121	1154.7	837.2	1140	971
5.5	140	−73.5	138	−52	412.7	210	401	273
6.0	44	−80.2	41	−74	146.2	17	138	44
6.5	13.7	−60.9	11	−62	51.3	−31.1	47	−38
7.0	4.1	−42.8	2	−45	17.8	−35.8	16	−23
8.0	0.28	−19.1	1	−23	2.09	−21	1	−31
9.0	−0.02	−8.7	1	−12	0.19	−10	−1	−19
30.0	0	0	0	0	0	0	0	0

[a] We have only compared to basis III results of SJ. All interaction potentials are expressed in μH

Table 3. Excitation cross sections in a_0^2

E (K)	$\sigma_{0\to1}$	$\sigma_{0\to2}$	$\sigma_{1\to2}$
25	0.14		
30	0.36		
35	0.70		
40	1.23		
45	2.09		
50	3.51		
60	11.7		
65	13.1	17.1	16.0
70	12.1	26.9	24.6
75	11.8	34.4	30.7
80	11.7	40.6	35.2
100	11.7	57.1	44.3
120	12.1	65.5	49.2
140	12.5	69.5	50.4
160	12.9	70.7	50.1
180	13.3	70.3	49.1
200	13.6	68.9	47.8
250	14.5	64.0	44.3
300	15.2	59.2	41.6
350	15.7	55.8	40.1
400	16.0	54.1	39.7
450	16.1	53.8	40.2
500	16.2	54.4	41.1
600	16.0	56.9	43.4
700	15.7	59.6	45.6
800	15.4	61.7	47.1
900	15.1	63.0	48.1
1000	14.9	63.8	48.6
1500	14.4	61.8	47.4
2000	14.9	54.7	43.0
3000	16.3	47.5	39.6
4000	17.0	47.9	40.3
5000	17.6	44.0	37.9
7500	18.0	43.3	38.1

Table 4. Averaged cross-sections in cm^2

T (K)	$\langle\sigma_{0\to1}\rangle$	$\langle\sigma_{0\to2}\rangle$	$\langle\sigma_{1\to2}\rangle$
10	1.62(−17)	1.13(−17)	6.99(−17)
20	9.65(−17)	2.05(−16)	4.05(−16)
30	1.68(−16)	5.14(−16)	6.90(−16)
40	2.19(−16)	7.90(−16)	8.74(−16)
45	2.38(−16)	9.04(−16)	9.38(−16)
50	2.55(−16)	1.00(−15)	9.88(−16)
60	2.81(−16)	1.16(−15)	1.06(−15)
70	3.02(−16)	1.27(−15)	1.11(−15)
80	3.19(−16)	1.35(−15)	1.13(−15)
90	3.33(−16)	1.41(−15)	1.15(−15)
100	3.44(−16)	1.46(−15)	1.17(−15)
150	3.81(−16)	1.56(−15)	1.19(−15)
200	4.00(−16)	1.60(−15)	1.21(−15)
250	4.09(−16)	1.62(−15)	1.22(−15)
300	4.14(−16)	1.64(−15)	1.24(−15)
400	4.18(−16)	1.65(−15)	1.25(−15)
500	4.20(−16)	1.65(−15)	1.26(−15)

corresponds to the lowest energy. Our calculations show however that this transition, although small, is the only possible up to kinetic energies of about 65 K since the $j=2$ channel is then closed and is of the same order of magnitude than the other cross-sections at upper energies.

We have performed the maxwellian average of the cross sections and give the corresponding results in Table 4.

$$\langle\sigma_{i\to j}\rangle=\left(\frac{1}{kT}\right)^2\int\sigma_{i\to j}(E)\varepsilon\exp(\varepsilon/kT)\,\mathrm{d}\varepsilon$$

where ε denotes the kinetic energy on level i, E is the total energy (kinetic + internal) and k is the Boltzmann's constant. This gives the respective role of the different fine structure transitions at the low temperatures relevant to the molecular clouds where the [C I] transitions are observed.

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Table 5. Fine structure excitation rate coefficients in $cm^3\ s^{-1}$

T (K)	$k_{0\to1}$	$k_{0\to2}$	$k_{1\to2}$
10	4.30(−13)	2.98(−13)	1.85(−12)
20	3.61(−12)	7.67(−12)	1.52(−11)
30	7.72(−12)	2.35(−11)	3.16(−11)
40	1.16(−11)	4.18(−11)	4.63(−11)
45	1.34(−11)	5.07(−11)	5.27(−11)
50	1.51(−11)	5.93(−11)	5.85(−11)
60	1.82(−11)	7.51(−11)	6.87(−11)
70	2.12(−11)	8.90(−11)	7.74(−11)
80	2.39(−11)	1.01(−10)	8.49(−11)
90	2.64(−11)	1.12(−10)	9.15(−11)
100	2.88(−11)	1.23(−10)	9.75(−11)
150	3.91(−11)	1.60(−10)	1.22(−10)
200	4.73(−11)	1.90(−10)	1.43(−10)
250	5.41(−11)	2.15(−10)	1.62(−10)
300	6.00(−11)	2.37(−10)	1.79(−10)
400	7.00(−11)	2.76(−10)	2.09(−10)
500	7.86(−10)	3.08(−10)	2.35(−10)

Table 6. Cooling functions in ergs $cm^3\ s^{-1}$

T (K)	C-H[a]	C-He[b]
10	1.58(−25)	3.91(−27)
20	6.82(−25)	6.68(−26)
30	1.42(−24)	2.26(−25)
40	1.73(−24)	3.94(−25)
50	2.14(−24)	5.55(−25)
60	2.54(−24)	7.00(−25)
70	2.76(−24)	8.29(−25)
80	3.00(−24)	9.42(−25)
90	3.20(−24)	1.04(−24)
100	3.41(−24)	1.13(−24)
200	4.70(−24)	1.77(−24)
300	5.58(−24)	2.22(−24)
400	6.28(−24)	2.59(−24)
500	6.88(−24)	2.89(−24)

[a] From Launay & Roueff (1977)
[b] Present work

The excitation rate coefficients which are expressed by:

$$k_{i\to j}=\sqrt{\frac{8kT}{\pi\mu}}\langle\sigma_{i\to j}\rangle$$

are given in Table 5 as a function of temperature.

The cooling efficiency coefficient $L(T)$:

$$L(T)=\sum_j \Delta E_{j\to 0}k_{0\to j}$$

is then calculated.

Table 6 gives the respective contributions of H and He to the cooling efficiency function of C I from Launay & Roueff (1977) and this work. These calculations should enable to help to estimate the contributions of molecular hydrogen to the excitation of C I as has already been done for the rotational excitation of CO. One can notice at this point the ratio of the 0→2 to 0→1 excitation rates of C by He which is found to be 3.6 at 45 K whereas Black et al. (1978) have concluded that this ratio should be between 1.8 and 3.5 for excitation by molecular hydrogen in their analysis of the relative populations of the C^3P_J levels in the cloud located in front of ζ Per.

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