

Excitation of the $C(2p^2\ ^3P_J)$ fine structure states in collisions with $He(1s^2\ ^1S_0)$

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Abstract. We have performed quantal calculations of the $^3\Sigma^-$ and $^3\Pi$ potential energy curves for interactions of C and He atoms in their ground states. The corresponding cross sections for transitions between the fine structure levels of C have also been determined. Rate coefficients are tabulated for these transitions in the temperature range $10 \leq T \leq 150$ K, relevant to studies of the interstellar medium.

1. Introduction

The excitation of fine structure transitions in collisions between atoms is an example of diabatic collision phenomena, involving more than one potential energy curve of the quasi-molecule. At low collision energies, the behaviour of the potential curves in the vicinity of the van der Waals minimum profoundly affects the magnitudes of the collision cross sections. As is well known, this region of the interaction is also the most difficult to calculate accurately, depending as it does on the compensation of weak, long-range (attractive) forces by short-range (repulsive) forces.

Whilst the theory of fine structure excitation in collisions with rare gases has existed for some time (Mies 1973, Reid 1973), both the number of systems amenable to theoretical study and the accuracy of such studies have been limited by the available *ab initio* potential energy curves. Thus, calculations of the $^3\Sigma^-$ and $^3\Pi$ interactions between $O(2p^4\ ^3P)$ and $He(1s^2\ ^1S)$ (Staemmler and Jaquet 1985) made possible the computations of elastic (Aquilanti *et al* 1986) and inelastic (Monteiro and Flower 1987) scattering cross sections. Until very recently, the analogous studies of the $C(2p^2\ ^3P)-He(1s^2\ ^1S)$ system had not been made, but two independent calculations have now been carried out. Lavendy *et al* (1991) have performed SCF+CI computations of the $^3\Sigma^-$ and $^3\Pi$ potentials, from which the cross sections for excitation of the $C(^3P_J)$ fine structure states by He have been determined. In the present paper, SCF+CEPA results for these same potentials and the corresponding excitation cross sections are presented. Comparison with the work of Lavendy *et al* shows that the interaction potentials are in good agreement at the SCF level but that the correlation contributions to the total interaction energies exhibit significant differences. These differences in the potentials and their consequences for the magnitudes of the inelastic collision cross sections are discussed. Rate coefficients, obtained as Maxwell averages over the velocity of collision, are tabulated against the kinetic temperature. These latter results are relevant to the interpretation of the $[C\ I]\ ^3P_1 \rightarrow ^3P_0$ and $^3P_2 \rightarrow ^3P_1$ emission lines observed

in the interstellar medium. Although H_2 , rather than He, is likely to be the principal collision partner in the interstellar gas, para- H_2 in its rotational ground state ($j=0$) may behave similarly to He, as is believed to be the case in collisions with $\text{O}(^3\text{P}_j)$ (Flower 1990). In fact, quantal calculations for the $\text{C}(2\text{p}^2\ ^3\text{P})\text{-H}_2$ and $\text{O}(2\text{p}^4\ ^3\text{P})\text{-H}_2$ systems are underway, and cross sections for excitation of the fine structure transitions by both para- and ortho- H_2 will be reported at a later date (Schröder *et al* 1991, Jaquet *et al* 1991).

2. Interaction potentials

The *ab initio* calculations of the interaction potential between $\text{C}(^3\text{P})$ and $\text{He}(^1\text{S})$ have been performed with the Bochum open-shell CEPA program package (Staemmler and Jaquet 1981) which has been used already for the calculation of the O-He potentials (Staemmler and Jaquet 1985). The first step is a restricted single-configuration SCF calculation which is followed by a CI with all singles and doubles (CI-SD) using the technique of pair natural orbitals (PNOs). The size consistency of the total energy which is necessary for a correct dissociation is achieved by the coupled electron pair approximation (CEPA, Meyer 1971). We have used a CEPA-2 (Meyer 1974) estimate of the unlinked cluster contributions (CEPA-SD). For the details of the method we refer to Staemmler and Jaquet (1981, 1985).

The following truncation thresholds have been used for the present calculations on C-He:

- (i) neglect of atomic integrals: $0.02\ \mu\text{H}$;
- (ii) convergence of the SCF iterations: $0.001\ \mu\text{H}$ for the energy;
- (iii) truncation of the PNO expansion: $0.1\ \mu\text{H}$ for the energy contribution, no additional truncation on the number of PNOs.

Using these thresholds, we estimate that the scatter in the calculated interaction energies, which is due mainly to the use of the truncated PNO expansion, is of the order of $0.2\text{--}0.5\ \mu\text{H}$; this is small compared with the interaction energies themselves and compared with the deficiencies of the finite basis set. The 1s electrons at the C atom were not correlated.

Contracted Gaussian lobe functions have been used throughout; full information about the basis set is given in table 1. We started from an 11s7p Huzinaga (1971) set, contracted to 7s5p, for the C atom and an 8s Huzinaga (1965) set, contracted to 6s, for the He atom. This set is similar to the one used by Lavendy *et al* (1991) for C-He, but more extended than the 9s5p set used previously for O-He (Staemmler and Jaquet 1985). The SCF basis set superposition error (BSSE) is considerably decreased if an 11s7p set is taken instead of the 9s5p set, but the change in the interaction energy after the counterpoise correction has been applied (see below) is very small.

This sp set has been augmented by diffuse s and p functions, to describe better the long-range part of the SCF wavefunction, and by several sets of polarization functions to take care of dispersion effects. All exponents are given in table 1. The potential curves were calculated with basis B; basis A was used only for basis tests and calibration. The exponents of the d, f, and g functions at C were roughly optimized: the range of exponents of the 'standard' set of Ahlrichs *et al* (1975) was extended to both sides, which turned out to be the best compromise: larger d exponents gave larger absolute correlation energies (i.e. larger intra-atomic correlation) but less dispersion, smaller exponents much less intra-atomic correlation and slightly ($\sim 1\ \mu\text{H}$ at $R = 7.0\ a_0$) more dispersion. The exponents for He were taken from Wasilewski *et al* (1988).

Table 1. Basis sets for C-He.

Basis	Atom	sp part ^a	Additional functions
A	C	11,7 \rightarrow 7,5	d(1.0, 0.3); f(0.8) ^b
	He	8 \rightarrow 6	s(0.048); p(2.5, 0.7, 0.2, 0.058); d(0.5, 0.15) ^c
B	C	11,7 \rightarrow 7,5	s(0.04); p(0.03); d(1.2, 0.4, 0.15); f(1.0, 0.3); g(0.3) ^d
	He	8 \rightarrow 6	s(0.048); p(2.5, 0.7, 0.2, 0.058); d(0.5, 0.15); f(0.3)

^a Exponents and contraction coefficients from Huzinaga (1965, 1971). Contraction pattern: 5,6 \times 1; 3,4 \times 1 for C and 3,5 \times 1 for He.

^b Polarization functions as optimized for the 'standard' basis in Ahlrichs *et al* (1975).

^c Wasilewski *et al* (1988).

^d Only σ , π , δ components of the full g set.

The asymptotic energies calculated with basis B are (in au): $C(^3P)$: -37.688 099 05 (SCF), -37.785 712 58 (CEPA-SD); $He(^1S)$: -2.861 609 74 (SCF), -2.899 033 18 (CEPA-SD). If we compare our calculated valence shell correlation energies of -0.0976 au ($C(^3P)$) and -0.0374 au ($He(^1S)$) with the best available values of -0.1024 au ($C(^3P)$; Bunge and Bunge 1970) and -0.0420 au ($He(^1S)$; Pekeris 1958), we see that our basis B is good for about 90% (He) to 95% (C) of the correlation effects; this gives a rough estimate of the errors to be expected for the dispersion energies.

We have calculated the static dipole polarizabilities of He and C using the finite field method first proposed by Cohen and Roothaan (1965). A homogeneous static electric field (field strengths of 10^{-3} - 10^{-2} au) was applied and the polarizability was evaluated as the first derivative of the induced dipole moment with respect to the field strength. Our result for α of the He atom calculated with basis B is (in au) 1.321 (SCF) and 1.381 (CEPA-SD), to be compared with the exact value of 1.383 (Buckingham and Hibbard 1968). For the C atom in its 3P ground state with the occupation $1s^2 2s^2 2p_x 2p_y$, we obtain with basis B: $\alpha_{zz} = \alpha_{\parallel} = 9.75$ (SCF), 9.84 (CEPA-SD); $\alpha_{xx} = \alpha_{\perp} = 12.64$ (SCF), 12.27 (CEPA-SD). The best available values are: $\alpha_{\parallel} = 10.14$ (SCF), 10.15 (PNO-CEPA); $\alpha_{\perp} = 13.09$ (SCF), 12.69 (PNO-CEPA) (Werner and Meyer 1976). Finally, the quadrupole moment of $C(^3P)$ is (in au) 1.542 (SCF) and 1.397 (CEPA-SD). It should be noted that in a CI (or CEPA) calculation with singles and doubles only, the SCF and not the CI values of the polarizabilities determine the size of the dispersion interaction. For both the He and C atoms, the SCF results for the polarizabilities are inaccurate by only a few per cent. The basis set used by Lavendy *et al* (1991) contains 2d on C and 4p1d on He and thus is even smaller than our basis A.

Our basis B used for the CEPA calculations of the interaction energies is not yet complete, and so the BSSE has to be taken into account. We have applied the Boys and Bernardi (1970) counterpoise correction; all the interaction energies given below are corrected with this recipe. The size of the BSSE at an intermediate distance ($R = 6.0 a_0$) is about $1 \mu H$ at the SCF level and about $20 \mu H$ at the CEPA-SD level (slightly different for the two states). This means that the SCF basis (sp part of basis B) is nearly saturated, but the BSSE is not negligible at the CEPA-SD level. The correlation

contribution to the interaction energies at $R = 6.0 a_0$ amounts to about $200 \mu\text{H}$ (see below, table 2), thus the BSSE with basis B renders the dispersion energies about 10% too large. Of course, this error is cancelled to some extent by the fact that basis B cannot fully describe the dispersion energy.

Table 2 contains our results for the C-He interaction potentials for the two states $^3\Sigma^-$ and $^3\Pi$. The $^3\Sigma^-$ state is less repulsive than the $^3\Pi$ state and exhibits a more pronounced minimum at a shorter internuclear separation. As Lavendy *et al* (1991) have pointed out, this behaviour is the consequence of the fact that, in the $^3\Sigma^-$ state, the 2p AO at the C-atom which points towards He is empty, but singly occupied in the $^3\Pi$ state. This effect is correctly described by the single-configuration SCF wavefunction ('SCF effect'). The small attraction in the $^3\Sigma^-$ state at the SCF level at large separation ($R > 8.0 a_0$) is an inductive minimum (quadrupole moment of C and induced dipole moment of He). Because of this inductive effect, the SCF interaction potential is not exponential in the $^3\Sigma^-$ state, while it is exponential in the $^3\Pi$ state. The SCF results of Lavendy *et al* (1991) are very close to ours; this is to be expected, since they employed a similar basis set.

The correlation contribution to the interaction energy (i.e. essentially the dispersion energy) in the two states is shown in a semilogarithmic plot in figure 1. The two curves are completely smooth and decay slightly faster than R^{-6} . For all distances the dispersion energy is larger (in absolute value) for the $^3\Pi$ state than for $^3\Sigma^-$: the ratio changes from 1.58 at $R = 3.5 a_0$ to 1.23 at $R = 9.0 a_0$. The reasons for this behaviour are: (a) α_\perp is about 30% larger than α_\parallel for the C atom, and α_\parallel is effective for $^3\Sigma^-$, α_\perp for $^3\Pi$; (b) in the $^3\Pi$ state one of the singly occupied 2p AOs of C(^3P) points towards He and is more strongly polarized than the two perpendicular 2p AOs.

In the calculations of Lavendy *et al* (1991), both the absolute values of the dispersion energy as well as $^3\Pi/^3\Sigma^-$ ratio are much smaller than in our calculation. One reason seems to be that we used a more extended atomic basis set. In some test calculations, we found that the $^3\Pi/^3\Sigma^-$ ratio of the dispersion energies did indeed decrease when

Table 2. C-He interaction potentials^{a,b}.

R	SCF		CEPA-SD	
	$^3\Sigma^-$	$^3\Pi$	$^3\Sigma^-$	$^3\Pi$
3.5	10 483.2	33 609.6	7 652.7	29 143.8
4.0	4 075.6	14 330.3	2 513.8	11 888.9
4.5	1 495.0	5 999.7	608.8	4 671.3
5.0	523.0	2 478.6	11.5	1 745.5
5.5	175.0	1 013.7	-127.4	584.7
6.0	55.7	411.4	-126.8	154.2
6.5	16.4	166.0	-95.5	10.4
7.0	4.2	66.7	-67.3	-30.2
7.5	0.6	26.7	-45.6	-34.8
8.0	-0.25	10.6	-31.4	-29.3
9.0	-0.29	1.66	-14.8	-16.2
10.0	-0.15	0.24	-7.6	-7.7
12.0	-0.04	-0.01	-2.2	-2.0
14.0	-0.01	0.00	-0.8	-0.4

^a Distances in a_0 , interaction energies in μH .

^b After counterpoise correction.

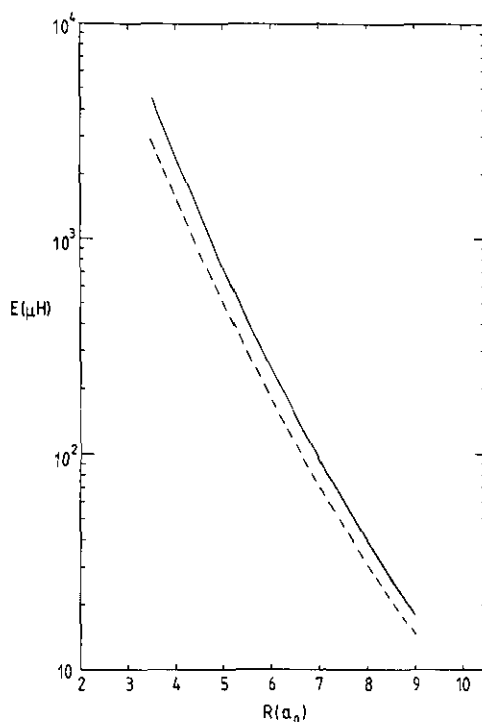


Figure 1. The correlation contributions to the interaction energies for the $^3\Sigma^-$ (broken curve) and $^3\Pi$ (full curve) potentials of C-He.

smaller basis sets were used. Furthermore, our CI space is also more complete than that of Lavendy *et al.*

In order to check the origin of this discrepancy, we have repeated the CEPA calculations for the internuclear distance $R = 7.0 a_0$ using the basis set of Lavendy *et al.* (1991). We obtained the following interaction energies (in μH), quoted in the sequence (a) Lavendy *et al.* (1991), (b) this work, their basis, without counterpoise correction, (c) this work, their basis, (d) this work, basis B (table 1): $^3\Sigma^-$, SCF: +1, -1, +4, +4; $^3\Pi$, SCF: +64, +64, +67, +67; $^3\Sigma^-$, CEPA: -48(CI), -72, -56, -67; $^3\Pi$, CEPA: +17(CI), -31, -10, -30. This comparison again shows that there is virtually no difference between our results and theirs at the SCF level. At the CI and CEPA level, the differences arise partly from the basis set (11 and 20 μH less attraction for $^3\Sigma^-$ and $^3\Pi$, respectively, in the CEPA calculations, using their basis, as compared with our basis B), but even more from the different treatment of correlation effects (discrepancies of 8 and 27 μH for $^3\Sigma^-$ and $^3\Pi$, respectively, between their CI and our CEPA, both with their basis). Accidentally, our CEPA results with their basis and without the counterpoise correction are virtually identical with our CEPA results using basis B, after the counterpoise correction; this is due to a cancellation of errors in the former treatment.

Since we did not aim at an accuracy better than 0.2–0.5 μH , it was not possible to extract C_6 , C_8 , C_{10} coefficients from the long-range part of our curves (Staemmler and Jaquet 1985). However, taking the C_6 coefficient for He_2 (-1.47 au, Tang *et al.* 1976) and an average value of the C_6 coefficients for C_2 (-32.0 au, Burke and Robb 1975), and using the combination rule

$$C_6^{AB} = \sqrt{C_6^{AA} C_6^{BB}}$$

one obtains $C_6^{\text{CHe}} = -6.86 \text{ au}$; this is quite close to the values of -7.9 au ($^3\Pi$) and -7.4 au ($^3\Sigma^-$) which derive from table 2 at $R = 10.0 a_0$ if C_8 and higher terms are neglected.

On the whole, we think that our SCF interaction potentials are converged to $1\text{--}2 \mu\text{H}$ with respect to the basis set limit, but the dispersion energies are probably 5–15% too small. Fortunately, it is the $^3\Sigma^- - ^3\Pi$ energy *difference* which determines the magnitudes of the fine structure excitation cross sections (see below).

3. Cross sections and rate coefficients

The collisional excitation of an atom in a ^3P state by a rare gas atom has been discussed by Aquilanti and Grossi (1980), Alexander *et al* (1983), Pouilly *et al* (1985), Aquilanti *et al* (1986), Monteiro and Flower (1987), and the theory will not be presented in detail here. These studies have shown that the inelastic (fine structure excitation) cross sections are determined directly by the magnitude of the difference, $V_{^3\Sigma^-} - V_{^3\Pi}$, between the $^3\Sigma^-$ and $^3\Pi$ potential energy curves. At low collision energies, the behaviour of this difference between the potentials and the depth of the Van der Waals minimum of the mean interaction, $(V_{^3\Sigma^-} + 2V_{^3\Pi})/3$, are of crucial importance. We note that $(V_{^3\Sigma^-} - V_{^3\Pi})$ has opposite sign for $\text{C}(^3\text{P})\text{--He}(^1\text{S})$ and $\text{O}(^3\text{P})\text{--He}(^1\text{S})$, C possessing two electrons in the 2p sub-shell, as compared with four in the case of O. Similarly, the $^3\text{P}_J$ levels in C form a normal triplet, whose energies ϵ_J satisfy $\epsilon_0 < \epsilon_1 < \epsilon_2$, whereas $\epsilon_0 > \epsilon_1 > \epsilon_2$ in O, corresponding to an inverted triplet. In the calculations for $\text{C}(^3\text{P}_J)$ reported below, we have adopted $\epsilon_0 = 0$, $\epsilon_1 = 16.4 \text{ cm}^{-1}$ and $\epsilon_2 = 43.4 \text{ cm}^{-1}$, consistent with the wavelengths of the observed interstellar lines (Phillips 1987).

The cross sections for the fine structure transitions were computed by the COLMOL program of Launay (1977), which is based upon the quantum-mechanical close-coupling approximation. The basis set consisted simply of the $^3\text{P}_J$ states of the C atom, giving rise to a maximum of five coupled channels of one parity and four of the other parity. In table 3 are listed the computed values of the de-excitation cross sections, $\sigma(J \rightarrow J')$, $J > J'$, as functions of the barycentric collision energy, E , relative to the $J = 0$ ground state. The cross sections for excitation may be obtained from the detailed balance relation

$$(2J+1)(E - \epsilon_J)\sigma(J \rightarrow J') = (2J'+1)(E - \epsilon_{J'})\sigma(J' \rightarrow J)$$

where $(E - \epsilon_J)$ and $(E - \epsilon_{J'})$ denote the collision energies relative to the respective initial states, J and J' , of the transitions. The corresponding results of Lavendy *et al* (1991) are also given in the table, for the purposes of comparison.

As may be seen from table 3, the values of $\sigma(2 \rightarrow 0)$ and $\sigma(2 \rightarrow 1)$ from these independent calculations agree tolerably well, particularly at the higher collision energies, whereas there are discrepancies for $\sigma(1 \rightarrow 0)$. We predict this cross section to be much larger in the region near threshold than is computed by Lavendy *et al* (1991). This difference in behaviour is attributable to the greater depth and proximity to the origin of the minimum of the mean interaction, $(V_{^3\Sigma^-} + 2V_{^3\Pi})/3$, in the present calculations. As discussed in section 2, we believe that the interaction potentials reported here are more accurate than those computed by Lavendy *et al* owing to a more complete basis set having been used to calculate the correlation contribution to the total energy.

The $J = 1 \rightarrow 0 = J'$ transition is driven only indirectly by the interaction potential, in the collisional sequence $J = 1 \rightarrow 2 \rightarrow 0 = J'$, as Alexander *et al* (1983) initially pointed out. For this reason, the behaviour of $\sigma(1 \rightarrow 0)$ near threshold is particularly sensitive

Table 3. Cross sections, σ , for transitions $J \rightarrow J'$ in C induced by He, as functions of the collision energy, E , relative to the $J = 0$ ground state; κ is Boltzmann's constant. (a) present work; (b) Lavendy *et al* (1991).

E/κ (K)	$\sigma(J \rightarrow J') \ a_0^2$					
	$1 \rightarrow 0$		$2 \rightarrow 0$		$2 \rightarrow 1$	
	(a)	(b)	(a)	(b)	(a)	(b)
25	5.39	0.83				
30	7.82	0.56				
40	9.75	1.0				
50	14.1	2.2				
60	23.8	6.4				
65	19.3	6.9	122	85.5	215	240
70	15.5	6.1	67.9	49.6	120	136
80	11.6	5.5	47.2	36.9	83.4	96.0
90	9.73		38.9		68.6	
100	8.63	5.1	34.0	30.4	59.9	70.7
120	7.41	5.0	28.0	27.3	49.7	61.5
140	6.76	5.0	24.3	25.1	43.5	54.6
160	6.38	5.0	21.7	23.2	39.1	49.3
180	6.14	5.1	19.6	21.5	35.8	45.1
200	5.97	5.1	18.0	20.0	33.3	41.7
300	5.60	5.5	13.3	14.9	26.3	31.5
400	5.45	5.7	11.6	12.8	24.2	28.2
600	5.20	5.6	11.4	12.7	25.3	29.1
800	4.99	5.3	12.2	13.4	27.3	30.7
1000	4.85	5.1	12.4	13.6	27.9	31.1

to the region of the van der Waals minimum. According to the present calculations of the potential energy curves for C-He, and those of Staemmler and Jaquet (1985) for O-He, the magnitude of the $^3\Sigma^- - ^3\Pi$ energy difference is larger in C-He than in O-He. As a consequence, the collisional 'selection rule' forbidding the direct $1 \rightarrow 0$ transition is less pronounced for C-He than for O-He collisions. For C-He, $\sigma(1 \rightarrow 0)$ decreases below the $J = 2$ threshold, where the collisional coupling between the $J = 1$ and $J = 2$ levels weakens.

Rate coefficients have been evaluated numerically as the Maxwell average, $\langle \sigma(J \rightarrow J')v \rangle$, of the cross section and the relative collision velocity, v , and are presented in table 4 for the de-excitation transitions, $J > J'$. For the reverse (excitation) transitions, the relation

$$(2J+1)\langle \sigma(J \rightarrow J')v \rangle = (2J'+1)\langle \sigma(J' \rightarrow J)v \rangle \exp[(\epsilon_J - \epsilon_{J'})/\kappa T]$$

may be used, where κ is Boltzmann's constant and T the kinetic temperature. Once again, the table provides a comparison with the corresponding results of Lavendy *et al*. Owing to the much larger values which we compute for the $1 \rightarrow 0$ cross section near threshold, the discrepancies are greatest at low temperatures for the $1 \rightarrow 0$ transition; at $T = 10$ K, the present study predicts a value of $\langle \sigma(1 \rightarrow 0)v \rangle$ which is larger by almost a factor of 6 than was computed by Lavendy *et al*. As T increases, the discrepancies between the two calculations decrease until, at $T = 150$ K, the results are in satisfactory agreement, consistent with the better accord between the cross sections at higher energies.

Table 4. Rate coefficients for fine structure transitions in C, induced by He, as functions of the kinetic temperature, T . (a) present work; (b) Lavendy *et al* (1991).

T (K)	$\langle \sigma(J \rightarrow J')v \rangle$ (10^{-11} cm ³ s ⁻¹)					
	1 \rightarrow 0		2 \rightarrow 0		2 \rightarrow 1	
	(a)	(b)	(a)	(b)	(a)	(b)
10	0.849	0.143	4.05	2.94	7.15	5.48
20	1.35	0.363	4.23	3.41	7.48	6.40
30	1.53	0.554	4.30	3.71	7.64	6.97
40	1.59	0.709	4.34	3.94	7.75	7.36
60	1.65	0.802	4.37	4.22	7.92	7.90
80	1.69	1.06	4.39	4.40	8.09	8.29
100	1.74	1.21	4.42	4.53	8.29	8.64
120	1.79		4.46		8.51	
150	1.86	1.52	4.53	4.84	8.83	9.52

From an analysis of observations of ζ Per, Black *et al* (1978) deduced that the rate coefficient for excitation of the $0 \rightarrow 2$ transition by molecular hydrogen at $T = 45$ K is between 1.8 and 3.5 times larger than for $0 \rightarrow 1$. The value which derives from our computations, for excitation by He, is approximately equal to their lower limit (1.8). As mentioned in the introduction, calculations of C-H₂ collisions are in progress.

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