

FINE-STRUCTURE EXCITATION OF O I AND C I BY IMPACT WITH ATOMIC HYDROGEN

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ABSTRACT

Using accurate interaction potentials, we perform refined calculations of rate coefficients for the fine-structure excitations in collisions of $O(^3P)$ and $C(^3P)$ with atomic hydrogen. The results are presented in the form of analytical functions approximating the rate coefficients over a wide range of temperatures. We examine the sensitivity of the collision dynamics to variations of the interaction potentials and the couplings to electronically excited states.

Subject headings: astrochemistry — atomic processes — methods: numerical — molecular processes — scattering

1. INTRODUCTION

The excitation of the fine-structure levels of O I and C I in collisions with hydrogen atoms contribute significantly to the cooling of diffuse interstellar gas (Dalgarno & McCray 1972; Cowie & Songaila 1986; Shaw et al. 2006). The intensities of the spectral lines that arise are also diagnostic probes of the environment of the atoms. The emission lines are strong in photon-dominated regions (PDRs; Kramer et al. 2004; Bernard-Salas & Tielens 2005; Bensch 2006). They have been used as mass tracers of galaxies (Papadopoulos & Greve 2004) and as indicators of the evolutionary stages of molecular clouds (Oka et al. 2004). The absorption line intensities provide a measure of the cosmic background temperature at high redshifts (Ge et al. 1997; Quast et al. 2002). The interpretation of the observational data depends on the rates of the excitation and deexcitation processes (Pequignot 1990).

The previous calculations of rate coefficients for fine-structure excitations in O-H and C-H collisions were reported by Launay & Roueff (1977). Their results were based on model interaction potentials and a sparse energy grid of cross sections. The interaction potentials of the OH and CH molecules that determine the collision problem have been calculated, subsequently, with much greater precision (Yarkony 1992; Parlant & Yarkony 1999; Kalemios et al. 1999) and a refined study of fine-structure excitation rates is warranted.

The interactions of $O(^3P)$ and $C(^3P)$ with hydrogen are determined by four molecular potentials of the $^2\Sigma$, $^2\Pi$, $^4\Sigma$, and $^4\Pi$ symmetries. These potentials have been recently computed by Parlant & Yarkony (1999) for the OH molecule and Kalemios et al. (1999) for the CH molecule. In this work, we use the results of Parlant & Yarkony and Kalemios et al. to improve on the calculations of Launay & Roueff (1977). We explore the sensitivity of the rate coefficients to the interaction potentials and present analytical formulae for the temperature dependence of the rate coefficients. The energy of the first electronic excitation of $O(^3P)$ to the 1D state is about 2 eV, and the 1D state is usually ignored in calculations of collision dynamics involving $O(^3P)$ at low temperatures. The interaction of $O(^1D)$ with hydrogen is, however, characterized by strongly attractive interaction potentials that are coupled to the $^2\Sigma$, $^2\Pi$, $^4\Sigma$, and $^4\Pi$ states of the OH molecule by the spin-orbit interaction (Krems et al. 2006) and may modify the dynamics of $O(^3P)$ -H collisions at high temperatures. We show that these couplings are insignificant.

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2. CALCULATION DETAILS

We calculate the cross sections for C-H and O-H collisions using the time-independent quantum mechanical approach as described by Launay (1977). The spin-orbit interaction splits the ground electronic state of oxygen and carbon into a triplet of fine-structure levels 3P_0 , 3P_1 , and 3P_2 . The lowest energy level of oxygen is 3P_2 and that of carbon is 3P_0 . Following the National Institute of Standards and Technology (NIST) database,¹ we adopt the energies 158 cm⁻¹ for the 3P_1 state and 227 cm⁻¹ for the 3P_0 state, relative to the 3P_2 state for oxygen. For carbon, we use the energies 16.4 cm⁻¹ for the 3P_1 state and 43.4 cm⁻¹ for the 3P_2 state, relative to the 3P_0 state. Within the close-coupling method (Arthurs & Dalgarno 1960) the scattering problem is reduced to a set of coupled second-order differential equations parameterized by the total energy and the total angular momentum of the collision complex. We solve these equations on a grid of 1450 kinetic energies in the interval from 1 to 10,000 cm⁻¹ and the total angular momenta $J = 0-100$. The solutions yield the scattering S -matrices and the cross sections for the fine-structure transitions (Launay 1977). The rate coefficients are calculated by averaging the product of the cross sections and the relative velocity over a Maxwellian velocity distribution. To generate the interaction potentials from the data of Parlant & Yarkony (1999), we used spline interpolation smoothly joined with the long-range analytical form of the interatomic interaction. The interaction potential data of Kalemios et al. (1999) were interpolated and extrapolated using the method described by Ho & Rabitz (1996).

3. RESULTS

Table 1 lists the rate coefficients for the fine-structure excitations in $C(^3P)$ -H collisions. The results in the “Accurate” columns are obtained using accurate interaction potentials of Kalemios et al. (1999). To estimate the uncertainties of our calculations and explore the sensitivity of the rate coefficients to the molecular potentials, we modified the short-range part of

¹ See <http://physics.nist.gov/PhysRefData/Handbook/index.html>.

TABLE 1
RATE COEFFICIENTS FOR THE FINE-STRUCTURE EXCITATIONS IN $C(^3P) + H$ COLLISIONS

T (K)	$k_{0 \rightarrow 1}$ ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)			$k_{0 \rightarrow 2}$ ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)			$k_{1 \rightarrow 2}$ ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)		
	LR77 ^a	Accurate ^b	Modified ^c	LR77 ^a	Accurate ^b	Modified ^c	LR77 ^a	Accurate ^b	Modified ^c
4.....	0.13	0.122	0.222	0.0191	...	0.0021	0.0340
5.....	0.42	0.382	0.609	...	0.0001	0.0239	...	0.0146	0.0508
7.....	1.64	1.40	2.16	...	0.0046	0.0367	0.15	0.132	0.190
8.....	2.51	2.10	3.23	...	0.0139	0.0491	0.30	0.261	0.345
9.....	3.51	2.87	4.42	...	0.0327	0.0701	0.52	0.444	0.568
10.....	4.59	3.68	5.67	0.10	0.065	0.103	0.80	0.678	0.857
12.....	6.87	5.33	8.23	0.27	0.180	0.218	1.54	1.28	1.61
14.....	9.17	6.93	10.70	0.57	0.3724	0.4084	2.45	2.02	2.55
20.....	15.20	11.08	16.95	2.14	1.39	1.43	5.76	4.61	5.90
30.....	22.20	16.00	23.87	6.00	4.00	4.14	11.40	9.03	11.52
40.....	26.50	19.44	28.18	10.00	7.035	7.343	16.20	13.02	16.37
70.....	33.80	25.86	35.16	19.20	16.08	16.86	26.20	22.59	27.04
100.....	38.00	29.75	38.97	25.10	23.83	24.90	32.40	29.79	34.43
200.....	45.20	37.56	46.38	37.40	41.19	42.71	44.50	45.20	49.71
250.....	47.50	40.41	49.12	42.10	46.94	48.62	48.70	50.41	54.92
300.....	48.90	42.90	51.53	46.20	51.70	53.51	52.40	54.79	59.33
400.....	51.80	47.12	55.68	53.20	59.45	61.46	58.80	62.06	66.70
500.....	54.60	50.68	59.20	59.10	65.80	67.94	64.30	68.12	72.86
700.....	59.60	56.67	65.12	68.80	76.20	78.46	73.70	78.24	83.07
800.....	62.00	59.32	67.70	73.00	80.67	82.92	77.80	82.65	87.48
900.....	64.20	61.80	70.08	76.90	84.80	87.00	81.70	86.75	91.52
1000.....	66.30	64.15	72.28	80.60	88.64	90.75	85.30	90.61	95.26

^a Data of Launay & Roueff (1977).

^b This work: accurate results.

^c This work: calculations with modified potentials.

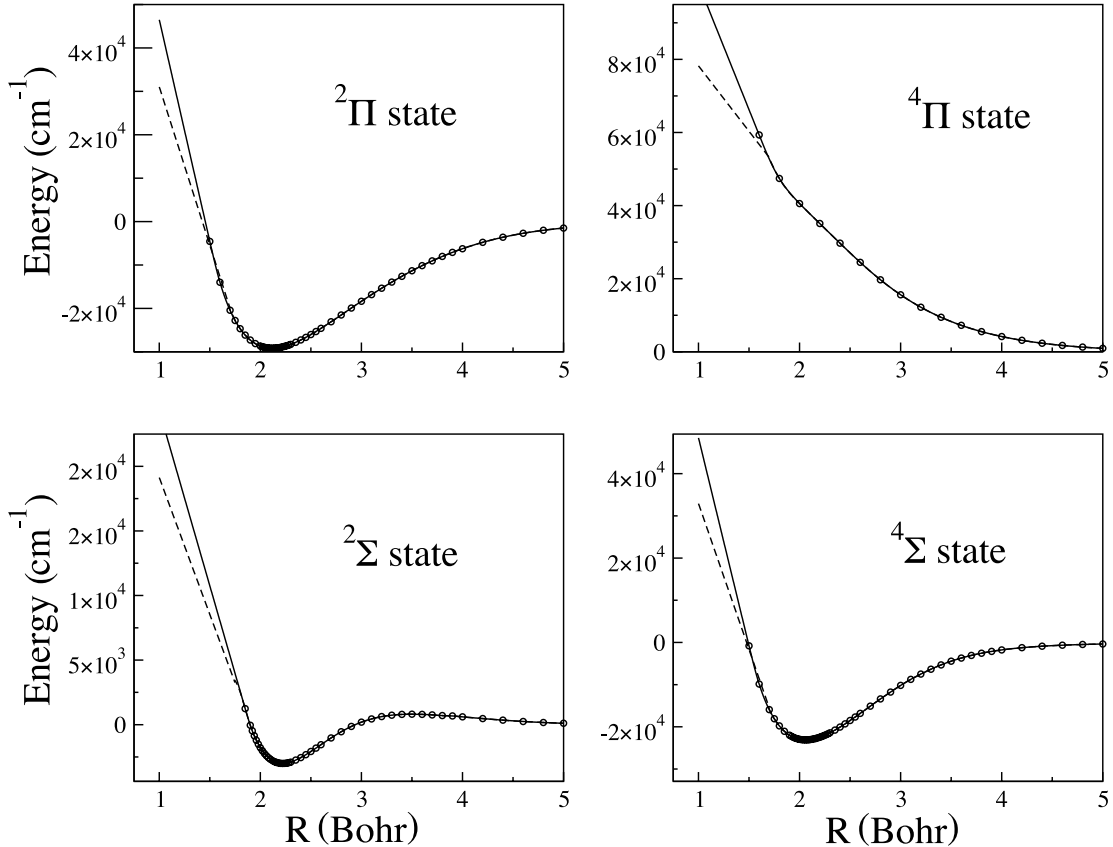


FIG. 1.—Interaction potentials of the $C(^3P)H$ molecule. *Circles*: ab initio calculations of Kalemios et al. (1999); *solid curves*: numerical interpolation of the ab initio data as described by Ho & Rabitz (1996); *dashed curves*: potentials with modified short-range interactions.

TABLE 2

FITTING COEFFICIENTS TO REPRESENT THE RATE COEFFICIENTS FOR THE FINE-STRUCTURE EXCITATIONS IN C + H COLLISIONS BY EQ. (1)

Excitation	$j = 0 \rightarrow j' = 1$	$j = 0 \rightarrow j' = 2$	$j = 1 \rightarrow j' = 2$
$a_{j \rightarrow j'}^{(0)}$	3.6593	10.8377	15.8996
$a_{j \rightarrow j'}^{(1)}$	56.6023	-173.4153	-201.3030
$a_{j \rightarrow j'}^{(2)}$	-802.9765	2024.0272	1533.6164
$a_{j \rightarrow j'}^{(3)}$	5025.1882	-13391.6549	-6491.0083
$a_{j \rightarrow j'}^{(4)}$	-17874.4255	52198.5522	15921.9239
$a_{j \rightarrow j'}^{(5)}$	38343.6655	-124518.3586	-22691.1632
$a_{j \rightarrow j'}^{(6)}$	-49249.4895	178182.5823	17334.7529
$a_{j \rightarrow j'}^{(7)}$	34789.3941	-140970.6106	-5517.9360
$a_{j \rightarrow j'}^{(8)}$	-10390.9809	47504.5861	0
b	1/4	1/3	1/4

the interaction potentials as shown in Figure 1. The dashed curves of Figure 1 are smoothly joined with the ab initio data at the interatomic distances $R > 1.7$ bohr. The “Modified” columns of Table 1 list the rate coefficients calculated with the modified potentials. Our results differ from the previous calculations of Launay & Roueff (1977) by up to 20% at low temperatures and agree well with their data at temperatures above 700 K. Given the model nature of the interaction potentials used by Launay & Roueff (1977) and the sensitivity of the dynamics to the interaction potentials demonstrated by Table 1, we find the agreement remarkable and coincidental.

At temperatures between 5 and 1000 K, the rate coefficients for the fine-structure excitations are accurately represented by the formula

$$\ln \left(\frac{k_{j \rightarrow j'}}{10^{-11}} \right) = \sum_{i=0}^N a_{j \rightarrow j'}^{(i)} T^{-ib}, \quad (1)$$

with the fitting coefficients listed in Table 2.

Table 3 presents the rate coefficients for the fine-structure excitations in O(³P)-H collisions. The calculations for oxygen are based on accurate interaction potentials computed and presented by Parlant & Yarkony (1999). The previous calculations

TABLE 4

FITTING COEFFICIENTS TO REPRESENT THE RATE COEFFICIENTS FOR THE FINE-STRUCTURE EXCITATIONS IN O + H COLLISIONS BY EQ. (1)

Excitation	$j = 2 \rightarrow j' = 1$	$j = 2 \rightarrow j' = 0$	$j = 1 \rightarrow j' = 0$
$a_{j \rightarrow j'}^{(0)}$	4.581	3.297	3.437
$a_{j \rightarrow j'}^{(1)}$	-156.118	-168.382	17.443
$a_{j \rightarrow j'}^{(2)}$	2679.979	1844.099	-618.761
$a_{j \rightarrow j'}^{(3)}$	-78996.962	-68362.889	3757.156
$a_{j \rightarrow j'}^{(4)}$	1308323.468	1376864.737	-12736.468
$a_{j \rightarrow j'}^{(5)}$	-13011761.861	-17964610.169	22785.266
$a_{j \rightarrow j'}^{(6)}$	71010784.971	134374927.808	-22759.228
$a_{j \rightarrow j'}^{(7)}$	-162826621.855	-430107587.886	12668.261
b	3/4	3/4	1/2

of Launay & Roueff (1977) underestimate our more accurate results by up to a factor of 4 at low temperatures and a factor of 2–3 at temperatures near 1000 K. At temperatures between 30 and 1000 K, the rate coefficients of Table 3 are accurately represented by equation (1) with the fitting coefficients listed in Table 4. For temperatures below 30 K the rate coefficients are less than 10^{-14} cm³ s⁻¹.

The energy of the first electronic excitation of O(³P) to the ¹D state is about 2 eV and the calculations of the fine-structure excitation rates reported here and previously (Launay & Roueff 1977) were performed with the basis set neglecting the electronic excited state of oxygen. The interaction of O(¹D) with H is described by three interaction potentials: $A^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ (Krems et al. 2006). The $A^2\Sigma^+$ potential is strongly attractive. The spin-orbit and Coriolis interactions couple the $A^2\Sigma^+$ state with the molecular states $^2\Sigma$, $^2\Pi$, $^4\Sigma$, and $^4\Pi$ that determine the collision dynamics of O(³P). The $^2\Sigma$, $^2\Pi$, $^4\Sigma$, and $^4\Pi$ states cross with the $A^2\Sigma^+$ state at energies between 4000 and 10,000 cm⁻¹, and the couplings to the ¹D state may modify the dynamics of O(³P)-H collisions. To verify the accuracy of our calculations and explore the role of the couplings to the ¹D state, we have written an independent computer program as described by Krems et al. (2006). Figure 2 compares the results of the extended calculations including the ¹D state with the cross sections

TABLE 3
RATE COEFFICIENTS FOR THE FINE-STRUCTURE EXCITATIONS IN O(³P) + H COLLISIONS

T (K)	$k_{2 \rightarrow 1}$ (10^{-11} cm ³ s ⁻¹)		$k_{2 \rightarrow 0}$ (10^{-11} cm ³ s ⁻¹)		$k_{1 \rightarrow 0}$ (10^{-11} cm ³ s ⁻¹)	
	LR77 ^a	This Work	LR77 ^a	This Work	LR77 ^a	This Work
50.....	...	0.189	...	0.0080	0.39	1.10
70.....	...	0.740	...	0.0548	...	2.70
100.....	0.56	2.20	...	0.243	1.33	5.38
150.....	1.66	5.49	0.13	0.827	2.13	9.89
200.....	2.98	9.06	0.29	1.59	2.81	13.80
250.....	4.37	12.54	0.49	2.42	3.39	17.02
300.....	5.74	15.83	0.71	3.24	3.92	19.65
350.....	7.06	18.90	0.94	4.04	4.40	21.79
400.....	8.33	21.74	1.18	4.80	4.85	23.55
450.....	9.54	24.36	1.42	5.51	5.28	25.00
500.....	10.69	26.79	1.66	6.18	5.69	26.21
600.....	12.80	31.14	2.13	7.40	6.48	28.11
700.....	14.80	34.91	2.57	8.47	7.21	29.49
800.....	16.60	38.22	3.00	9.41	7.91	30.55
900.....	18.30	41.14	3.41	10.25	8.58	31.37
1000.....	19.90	43.75	3.80	11.01	9.22	32.03

^a Data of Launay & Roueff (1977).

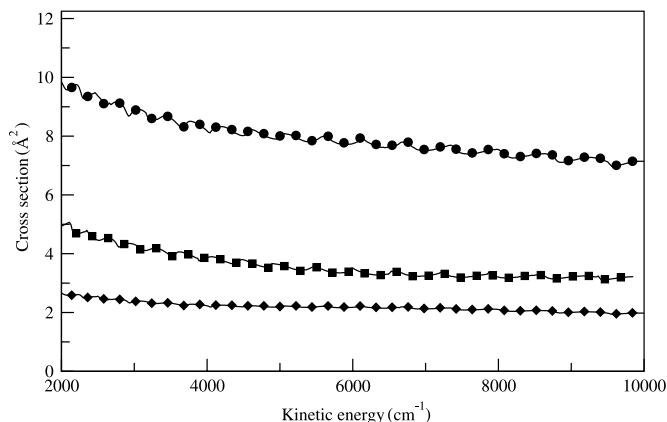


FIG. 2.— Cross sections for the fine-structure excitations in $O(^3P)$ -H collisions. Circles: $j = 2 \rightarrow j = 1$ transition; squares: $j = 1 \rightarrow j = 0$ transition; diamonds: $j = 2 \rightarrow j = 0$ transition. Solid curves represent calculations including the 1D state of oxygen as described by Krems et al. (2006).

computed using the conventional basis set of only the 3P states. The couplings to the 1D state appear to be insignificant even at high collision energies of $10,000 \text{ cm}^{-1}$.

4. SUMMARY

Using accurate interaction potentials of Parlant & Yarkony (1999) and Kalemoss et al. (1999), we have recalculated the rate

coefficients for the fine-structure excitations in collisions of $O(^3P)$ and $C(^3P)$ with atomic hydrogen. The results are presented in the form of analytical functions representing the rate coefficients over a wide range of temperatures. To verify the accuracy of the calculations, we examined the sensitivity of the rate coefficients to variations of the interaction potentials at short range and the couplings to electronically excited states of oxygen. This is the first calculation of fine-structure excitation dynamics of $O(^3P)$ with the couplings to the 1D states included. Given the recent progress in interstellar spectroscopy measurements, the refined results presented here may improve our understanding of the conditions in the interstellar medium.

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