

Solar Photodetachment Rates of Monatomic Anions

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Abstract

The solar detachment rates of all stable atomic anions belonging to elements in the main body of the periodic table have been calculated. Multi-channel photodetachment effects owing to fine structure levels and temperature effects are included in the treatment. All told the solar detachment rates of 31 anions at 300 and 10^4 K are made available. The rates show strong correlation to the group number in the periodic table. The higher the group number of the element, the lower is its detachment rate. Caesium has the highest detachment rate of 82 s^{-1} , while fluorine has the lowest rate of 0.069 s^{-1} . The calculations shown here may be useful to researchers conducting experiments on ionospheric modification where negative ions which are not normally found in the atmosphere may appear in abundance.

1. Introduction

The electron affinities of most atoms are approximately 1 eV. Hence a significant fraction of the photons in the solar spectrum is energetically capable of detaching an electron from an anion. Such a release of electrons from anions is referred to as the solar photodetachment process. This process is believed to be related to the rapid increase in the free electron density in the 60–80 km altitude region of the atmosphere at sunrise (Thomas and Harrison 1970), and to the large diurnal change in radio-wave absorption during polar cap absorption events (Bailey 1959).

Attempts have been made to measure or calculate the sunlight detachment rate of various atmospheric anions. Rates have been reported for O^- , 1.4 s^{-1} (Smith 1960); O_2^- , 0.4 s^{-1} (Smith *et al.* 1958) and $0.3 \pm 0.1\text{ s}^{-1}$ (Woo *et al.* 1969); O_3^- , $0.082 \pm 0.015\text{ s}^{-1}$ (Wong *et al.* 1972); CO_3^- , $0.022 \pm 0.003\text{ s}^{-1}$ (Hong *et al.* 1977); NO_2^- , $0.042 \pm 0.010\text{ s}^{-1}$ at 300 K and $0.048 \pm 0.012\text{ s}^{-1}$ at 2000 K (Woo *et al.* 1981).

Through the advancement of rocketry, it is now possible to conduct ionospheric modification experiments (Anderson and Mendillo 1983; Mendillo and Tyler 1983; Wand and Mendillo 1984). The purpose of these experiments is to study a variety of ionospheric properties by artificially inducing large-scale long-lived negative ions and creating regions of plasma depletion in the ionosphere. Hence, negative ions which are not normally found in the atmosphere may appear in abundance under such conditions of ionospheric modification. For example, I^- was the product ion of ionospheric modification experiments by Mendillo and Forbes (1982), when CF_3I was used as the attachment species (M. Mendillo, personal communication).

The determination of the solar detachment rate of many of the non-atmospheric anions as a function of temperature is difficult under laboratory conditions. On the other hand, calculations based on the versatile zero core-contribution (ZCC) approximation (Stehman and Woo 1979; Clodius *et al.* 1983) are relatively straightforward.

2. Theory

The ionospheric solar photodetachment rate (zero optical depth) as a function of temperature* is obtained from the integral

$$R(T) = \int \{s(\lambda) \lambda/hc\} \sigma(\lambda, T) d\lambda, \quad (1)$$

where $s(\lambda) \lambda/hc$ is the photon flux as a function of the wavelength and σ is the photodetachment cross section.

A ZCC calculation (Clodius 1982) shows that

$$\begin{aligned} \sigma(\lambda, T) = & \sum_{L,S,J} \sum_{L',S',J'} F(L, S, J, T) |\langle l^n(S', L') l \rangle LS \rangle|^2 \\ & \times B(l, L', S', J'; L, S, J) \sigma_1(l, L', S', J'; L, S, J; \lambda), \end{aligned} \quad (2)$$

where L , S and J are respectively the orbital, spin and total angular momentum of the anion, while their primed values are those of the neutral atom. The symbols $\langle l^n(S', L') l \rangle LS \rangle$, B and T are respectively the fractional parentage coefficient, the branching ratio (Clodius 1982) and the temperature, while l and n are the electron orbital angular momentum of the outermost shell of the anion and the number of electrons in the outermost shell of the neutral atom. The fraction of ion population $F(L, S, J, T)$ in a state of specified L , S , J and T is given by

$$\begin{aligned} F(L, S, J, T) \\ = (2J+1) \exp(-E_i(L, S, J)/k_B T) / \sum_{L,S,J} (2J+1) \exp(-E_i(L, S, J)/k_B T), \end{aligned} \quad (3)$$

where $E_i(L, S, J)$ is the excitation energy required to reach the i th excited state of the anion having the specified L , S and J , and the Boltzmann constant is k_B . The photodetachment cross section σ_1 depends on the value of l for the anion; its expressions for $l = 0$ and $l = 1$ are in Stehmann and Woo (1979) [equations (9), (12) and (14) for $l = 0$, equations (16), (17a), (17b) and (19) for $l = 1$].

3. Results

The formulas given in the previous section have been used to calculate rates for all the stable atomic anions belonging to elements contained in the main body of the periodic table. All told, the rates of 31 anions are calculated. Seven anions belong to Group 1 of the periodic table and have l values of zero. The 24 remaining anions belong to elements contained in Groups 3–7 of the periodic table and each has an l value of unity. Elements in Groups 2 and 8 and the nitrogen atom of Group 5 do not form stable anions.

* Here R is used for the rate instead of the SI symbol J , since J is used for the total angular momentum.

Table 1. Solar detachment rates R_1 and R_2 and parameters required for their calculation

Element	r_0^A	E_A^B	Excitation energies of higher ionic states ^D				Excitation energies of higher atomic states ^E				R_1^F	R_2^G	
Group 1 elements													
			1S_0		$^2S_{1/2}$								
H	1.55	0.75									19.8		
Li	2.81	0.62									49.1		
Na	3.00	0.55									56.0		
K	3.65	0.50									71.2		
Rb	3.84	0.49									75.3		
Cs	4.16	0.47									82.1		
Pr	4.07	0.46									80.1		
Group 3 elements													
			3P_0	3P_1	3P_2	$^2P_{1/2}$	$^2P_{3/2}$						
B	1.78	0.28		0.001	0.003		0.002					20.0	20.0
Al	2.61	0.44 ^C		0.003	0.006 ^C		0.014					32.3	32.3
Ga	2.56	0.30		0.027	0.072		0.103					33.6	33.7
In	2.70	0.30		0.085	0.192		0.275					35.3	35.7
Tl	2.55	0.30					0.968					25.3	
Group 4 elements													
			$^4S_{3/2}$	$^2D_{3/2}$	$^2D_{5/2}$	3P_0	3P_1	3P_2	1D_2	1S_0			
C	1.35	1.27					0.002	0.005	1.27	2.69	4.45		
Si	2.05	1.39		0.86	0.86		0.010	0.028	0.782	1.91	8.32	11.4	
Ge	2.11	1.20		0.78	0.80		0.069	0.175	0.885	2.03	9.53	12.5	
Sn	2.29	1.25		0.65	0.75		0.210	0.426	1.07	2.13	8.62	11.1	
Pb	2.23	0.37 ^C					0.971	1.32	2.66	3.66	10.3		
Group 5 elements													
			3P_2	3P_1	3P_0	$^4S_{3/2}$	$^2D_{3/2}$	$^2D_{5/2}$	$^2P_{1/2}$	$^2P_{3/2}$			
P	1.73	0.75		0.023	0.033		1.47	1.48	2.33	2.33	5.57	5.61	
As	1.87	0.80		0.136	0.186		1.32	1.36	2.26	2.32	5.74	6.16	
Sb	2.15	1.05		0.335	0.372		1.06	1.22	2.04	2.29	5.76	6.78	
Bi	2.37	0.95 ^C		0.6	0.65		1.42	1.92	2.69	4.12	6.60	8.48	
Group 6 elements													
			$^2P_{3/2}$	$^2P_{1/2}$		3P_2	3P_1	3P_0	1D_2	1S_0			
O	0.96	1.46		0.022			0.02	0.028	1.97	4.20	1.23	1.23	
S	1.51	2.08		0.07			0.049	0.071	1.15	2.75	1.29	1.31	
Se	1.66	2.02		0.283			0.247	0.315	1.19	2.79	1.59	1.70	
Te	1.94	1.97		0.622			0.59	0.584	1.31	2.88	2.02	2.30	
Po	2.13	1.9					2.09	0.933	2.69		2.15		
Group 7 elements													
			1S_0		$^2P_{3/2}$	$^2P_{1/2}$							
F	0.84	3.40				0.05					0.069		
Cl	1.34	3.62				0.11					0.092		
Br	1.52	3.36				0.46					0.174		
I	1.79	3.06				0.94					0.382		
At	1.97	2.80				3.84					0.706		

^A Core radius of anion ($\text{\AA} = 10^{-10} \text{ m}$); $r_0 = 1.3 \langle R^2 \rangle^{\frac{1}{2}}$ ($\langle R^2 \rangle^{\frac{1}{2}}$ from Lu *et al.* 1971).

^B Electron affinity of atoms (eV) from Hotop and Lineberger (1975) and Clodius *et al.* (1983) unless otherwise specified.

^c From Feigerle *et al.* (1981). Brunot *et al.* (1981) report $E_A = 1.2 \pm 0.1$ eV for Pb.

^D Units in eV. From Clodius (1982) unless otherwise specified.

^E Units in eV. From Moore (1971).

^F Solar detachment rate (s⁻¹) at 300 K.

^G Solar detachment rate (s^{-1}) at 10^4 K.

Tables 1 and 2 provide the input parameters required for the calculation of the photodetachment cross sections and the resulting calculated solar detachment rates at 300 and 10⁴ K. The input parameters are the core radius of the anions, the electron affinities of the atoms, the excitation energies required to reach the higher states of the anions, the excitation energies required to reach the higher states of the neutral atoms (Table 1), the fractional parentage coefficients and the branching ratios

Table 2. Fractional parentage coefficient (FPC) and branching ratio *B* for ionic and atomic states of each group

Ionic state	Atomic state	FPC	<i>B</i>	Ionic state	Atomic state	FPC	<i>B</i>
Group 1				Group 5			
¹ S ₀	² S _{1/2}	1·0	1·0	³ P ₂	⁴ S _{3/2}	1/3	1·0
					² D _{3/2}	5/12	1/10
Group 3						² D _{5/2}	5/12
³ P ₀	² P _{1/2}	1·0	2/3		² P _{1/2}	1/4	1/6
	² P _{3/2}	1·0	1/3		² P _{3/2}	1/4	5/6
³ P ₁	² P _{1/2}	1·0	1/2	³ P ₁	⁴ S _{3/2}	1/3	1·0
	² P _{3/2}	1·0	1/2		² D _{3/2}	5/12	7/10
³ P ₂	² P _{1/2}	1·0	1/6			² D _{5/2}	5/12
	² P _{3/2}	1·0	5/6		² P _{1/2}	1/4	1/2
Group 4					² P _{3/2}	1/4	1/2
⁴ S _{3/2}	³ P ₀	1·0	1/9	³ P ₀	⁴ S _{3/2}	1/3	1·0
	³ P ₁	1·0	1/3		² D _{3/2}	5/12	1·0
	³ P ₂	1·0	5/9		² D _{5/2}	5/12	0
	¹ D ₂	0	0		² P _{1/2}	1/4	2/3
	¹ S ₀	0	0		² P _{3/2}	1/4	1/3
² D _{3/2}	³ P ₀	1/2	5/18	Group 6			
	³ P ₁	1/2	7/12	² P _{3/2}	³ P ₂	3/5	25/36
	³ P ₂	1/2	5/36		³ P ₁	3/5	1/4
	¹ D ₂	1/2	1·0		³ P ₀	3/5	1/18
² D _{5/2}	¹ S ₀	0	0		¹ D ₂	1/3	1·0
	³ P ₀	1/2	0		¹ S ₀	1/15	1·0
	³ P ₁	1/2	1/6	² P _{1/2}	³ P ₂	3/5	5/18
	³ P ₂	1/2	5/6		³ P ₁	3/5	1/2
	¹ D ₂	1/2	1·0		³ P ₀	3/5	2/9
	¹ S ₀	0	0		¹ D ₂	1/3	1·0
					¹ S ₀	1/15	1·0
				Group 7			
				¹ S ₀	² P _{3/2}	1·0	2/3
					² P _{1/2}	1·0	1/3

(Table 2). Anions from Groups 1 and 7 and anions of elements Tl, C, Pb and Po have only one stable ionic state and, consequently, their Boltzmann population distribution factor is unity regardless of the temperature. This makes their solar rates independent of temperature and they are, therefore, listed only once in Table 1 to avoid repetition. The choice of 10⁴ K is somewhat arbitrary and is intended to show that the solar detachment rates do not increase significantly even at such a high temperature.

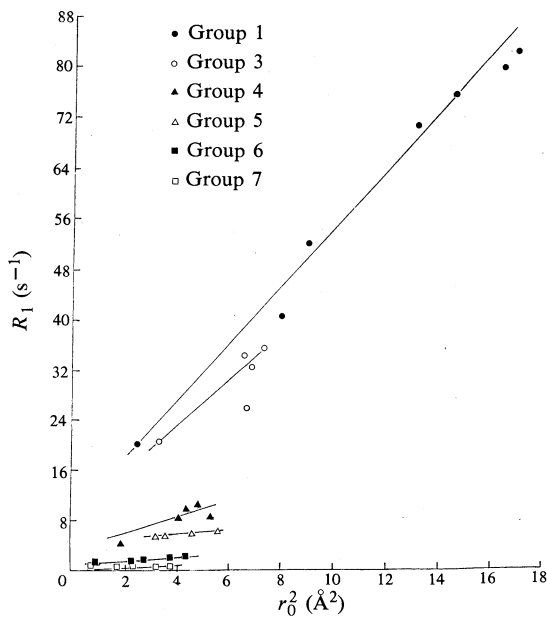


Fig. 1. Solar photodetachment rate R_1 at 300 K as a function of the square of the anion radius r_0 .

Fig. 2. Solar photodetachment rate as a function of group number C for a fixed atomic number $Z = 50$.

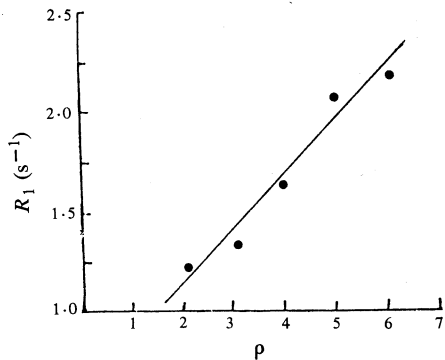
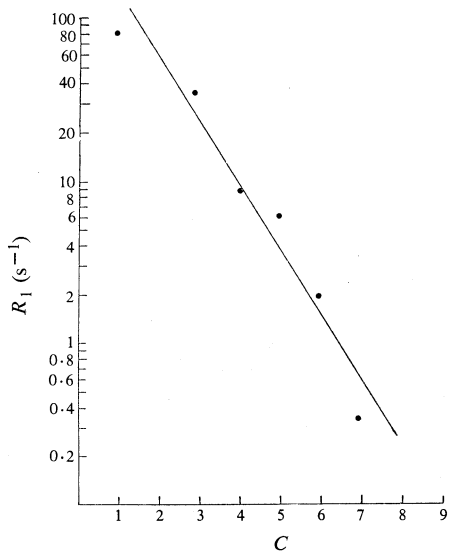


Fig. 3. Dependence of solar photodetachment rate on row number for Group 6.

4. Discussion

The data in Table 1 show that, contrary to common expectation, the electron affinity is not necessarily the primary factor which determines the size of the solar rate. For example, the electron affinities E_A of most elements in Groups 5 and 3 are lower than corresponding elements in Groups 4 and 1, yet their solar rates are about 50% smaller in comparison. Many factors including the fractional parentage coefficient and branching ratios combine to determine the size of the solar rate. In general, the radius of the neutral core, which affects the diffuseness of the electronic wavefunction of the anion, is at least as important as the electron affinity. The magnitudes of the solar rates at 300 K vary approximately as r_0^2 (see Fig. 1).

The dependence of the solar photodetachment rates on the atomic numbers of the elements can be seen from Table 1. At 300 K, the largest solar rate R_1 for an atomic anion is about 80 s^{-1} and the smallest is about 0.07 s^{-1} . The difference is about three orders of magnitude which is surprisingly large. Fig. 2 presents a semilog plot of the solar rate at 300 K as a function of the group number C . The values of the rates are correlated strongly with the group number. An increase of unity in the value of C causes a decrease in the rate by about a factor of two, i.e., $R_1 = 80/2^{C-1}$, where $C = 1, 3, 4-7$. The magnitude of the rate also depends slightly on the row position ρ . In general, for anions of the same group in the periodic table, the smaller the value of ρ , the smaller the solar rate will be. Fig. 3 shows this dependence for Group 6. An empirical formula, which embodies the characteristics mentioned above and which is accurate to within a factor of two to the calculated rates, can be written as

$$R_1 = \frac{80}{2 \cdot 3^{C+(1/C)-2}} \{1 - 0.01(7-\rho)(1.16)|C-3|\}, \quad (4)$$

where $C = 1, 3-7$ and $\rho = 1-7$. One might note that equation (4) has a maximum value of 80 s^{-1} at $C = 1$ and $\rho = 7$ and a minimum value of 0.09 s^{-1} at $C = 7$ and $\rho = 2$.

In order to understand why the solar rates of Te^- increase by 15% while those of many other anions do not, one may recall that its excited states are significantly higher in energy above the ground state (see Table 1). Hence, at high temperatures the excited ionic states are significantly populated which, in effect, lowers the electron affinity of the anion and which in turn provides a larger range of overlap between the solar flux and the photodetachment cross section, thereby yielding a larger solar rate. For anions whose fine structure splittings are low in energy compared with the room temperature thermal energy, such as B^- , P^- and O^- (Table 1), the effective lowering of the electron affinity at high temperatures is minimal. Their solar detachment rates stay practically constant with temperature.

The photodetachment cross sections calculated by the ZCC approximation were originally claimed to have an accuracy of $\pm 50\%$. However, comparison with the experimental data involving almost 30 atomic anions (Stehman and Woo 1979; Clodius *et al.* 1983) suggests strongly that the accuracy is probably better than $\pm 35\%$. In general, the smaller the uncertainties assigned to the experimental data, the better the agreement will be with the results of the ZCC approximation. The solar rates given here are probably even more accurate, since the accuracy of the solar photon flux is within a few per cent and the integration process involved in the evaluation

of the solar rate involves an averaging effect which will further increase the accuracy. Overall we estimate the accuracy of the rates to be $\pm 30\%$.

5. Conclusions

The solar photodetachment rates of all stable atomic anions belonging to elements in the main body of the periodic table have been evaluated, assuming zero optical depth and noon-time conditions. Their estimated accuracy is $\pm 30\%$.

The temperature dependence of the solar rates has been examined. Even at a temperature as high as 10^4 K, the effect is weak except for a few anions such as Si^- , Ge^- , Sn^- , Sb^- and Bi^- .

The solar rates for anions vary drastically in magnitude; for example, Cs^- has a solar rate of about 80 s^{-1} which shows that its mean lifetime, if controlled by photodetachment, is only 0.01 s in the ionosphere at noon. On the other hand, the mean lifetime of F^- (solar rate 0.069 s^{-1}), under the same conditions, is about 10 s .

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