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Fine-structure excitation of O^{2+} by charge transfer of O^{3+} in H at low energies

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A multistate molecular expansion is developed to describe the charge transfer of O^{3+} ions with neutral hydrogen atoms in which the individual fine-structure levels of the initial O^{3+} ion and the product O^{2+} states are taken into account. The coupled scattering equations are solved and cross sections are obtained for charge transfer excitation at energies near 1 eV.

I. INTRODUCTION

Calculations[1,2] have been carried out of the low-energy cross sections and thermal-rate coefficients for electron capture into excited states of O^{2+} by O^{3+} ions colliding with atomic hydrogen,

$$O^{3+}+H\rightarrow O^{2+}+H^{+} , \tag{1}$$

with results that are consistent with the measurements of the total cross sections.[3] The charge transfer processes were assumed to be driven by the nuclear radial coupling between the adiabatic electronic states of the quasimolecular ion formed during the collision. The electronic states are specified by the total electron spin S and the component Λ of electronic angular momentum along the nuclear axis. Cross sections were calculated for capture into specific spin and orbital angular momentum LS states of O^{2+}, and the resulting emission spectrum was obtained.[4,5] The theoretical method does not distinguish between the individual fine-structure levels of the initial or of the product ions. Emission lines from the individual fine-structure levels of excited states of O^{2+} have been identified in astrophysical plasmas,[6] but their interpretation is complicated by the existence of several excitation mechanisms.[5] Cross sections and rate coefficients for electron capture from and into specific fine-structure levels are needed to separate out the contributions from the charge transfer processes.

The earlier studies[1] showed that, at thermal energies, the major channels are capture into the $(2p3s,{}^1P^0)$, $(2p3p,{}^1P)$, $(2p3s,{}^3P^0)$, $(2p3p,{}^3D)$, and $(2p3p,{}^3S)$ LS states of O^{2+}. We retain these channels in a more general scattering theory which recognizes explicitly the fine-structure levels in the initial and final states and takes correct account of their energies. Each of the processes may be represented by

$$O^{3+}({}^2P_{1/2,3/2})+H\rightarrow O^{2+}({}^{2s_a'+1}L_a'j_a')+H^{+} . \tag{2}$$

II. SCATTERING THEORY

Heil *et al.*[7] calculated the adiabatic electronic Born-Oppenheimer eigenfunctions $\psi(\gamma\Lambda S\mid R)$ of the singlet and triplet Σ and Π states of OH^{3+} at internuclear distances R, the label γ distinguishing between different molecular states of the same symmetry. They also calculated the adiabatic potential-energy curves $V(\gamma\Lambda S\mid R)$ and the matrix elements

$$A(R)=\langle\psi(\gamma_1\Lambda S\mid R)\mid d/dR\mid\psi(\gamma_2\Lambda S\mid R\rangle$$

of the nuclear radial momentum operator which couples states of the same ΛS symmetry. Rotational couplings were neglected. To set up the scattering theory, the adiabatic basis was transformed to a diabatic representation.[8] In the diabatic representation, transitions are driven by the off-diagonal elements $V(\gamma\gamma'\Lambda S\mid R)$ of the diabatic potential matrix $\mathbf{V}(\Lambda S\mid R)$ which couple states with the same values of Λ and S. The diagonal elements of $\mathbf{V}$ are the diabatic potential-energy curves.

The initial approach of the $O^{3+}({}^2P)$ state and the $H({}^2S)$ state may occur in any one of the ${}^1\Sigma^+$, ${}^3\Sigma^+$, ${}^1\Pi$, and ${}^3\Pi$ molecular states. The cross section for any particular symmetry may be written[8]

$$\sigma_{\Lambda S}(\gamma,\gamma'\mid E)=\frac{\pi}{k_\gamma^2}\sum_J(2J+1)\mid T^J_{\Lambda S}(\gamma,\gamma')\mid^2 , \tag{3}$$

where $T^J_{\Lambda S}$ is the transition matrix element connecting the initial state $(\gamma\Lambda S)$ with the particular final state $(\gamma'\Lambda S)$ produced by charge transfer, J is the total angular momentum quantum number, and k_γ is the wave number of the initial relative motion. In terms of the energy E of relative motion,

$$k_\gamma^2=2\mu E/\hbar^2 , \tag{4}$$

where μ is the reduced mass.

The cross section for the charge transfer process

$$O^{3+}({}^2P)+H({}^2S)\rightarrow O^{2+}({}^{2s_a'+1}L_a')+H^{+} \tag{5}$$

is given by

$$\sigma(L_as_a;L_a's_a')=\sum_{\Lambda S}\frac{(2-\delta_{0,\Lambda})(2S+1)}{(2L_a+1)(2s_a+1)(2s_b+1)}\sigma_{\Lambda S} , \tag{6}$$

where $L_a=1$, $s_a=\frac{1}{2}$, $s_b=\frac{1}{2}$, and the total spin $S=s_a \pm s_b = s_a'$.

The generalization of the theory to take account of electron capture into fine-structure levels is a straightforward extension of the theory of direct fine-structure excitation.[9,10] We employ the formulation of Chambaud *et al.*[10]

We consider the collision of an atom A with orbital, spin, and total electronic angular momentum L_a, s_a, and j_a, respectively, with an atom B with orbital, spin, and total electronic angular momentum L_b, s_b, and j_b, respectively. The total electronic angular momentum of the collision system is $\mathbf{j}=\mathbf{j}_a+\mathbf{j}_b$. Let $\mathbf{l}$ be the orbital angular momentum of the relative nuclear motion, and write $\mathbf{J}=\mathbf{j}+\mathbf{l}$ for the total angular momentum of the collision system. The corresponding total angular momentum eigenfunctions may be written

$$|\gamma(L_a s_a)j_a(L_b s_b)j_b jl \,|\, JM\rangle \ ,$$

where γ is a label identifying the specific atomic states into which the system separates and M is the projection of $\mathbf{J}$ onto the space-fixed z axis.

The cross section for the transition from $(\gamma j_a j_b)$ to $(\gamma' j_a' j_b')$ may be written

$$\sigma(\gamma j_a j_b;\gamma' j_a' j_b')=\frac{\pi}{(2j_a+1)(2j_b+1)k_\gamma^2}\sum_{J,l,l'}(2J+1)\,|\,T^J(\gamma j_a j_b l;\gamma' j_a' j_b' l')\,|^2 \ , \tag{7}$$

where the transition matrix is obtained from the asymptotic solution of a set of coupled partial-wave equations. The cross section for transitions from the initial LS terms $(\gamma L_a s_a L_b s_b)$ to the final terms $(\gamma' L_a' s_a' L_b' s_b')$ is obtained by averaging over the initial states $(\gamma j_a \gamma_b)$ and summing over the final states $(\gamma j_a' j_b')$. Thus

$$\sigma(\gamma L_a s_a L_b s_b;\gamma' L_a' s_a' L_b' s_b')=\frac{1}{(2L_a+1)(2s_a+1)(2L_b+1)(2s_b+1)}\sum_{j_a,j_a'}(2j_a+1)(2j_b+1)\sigma(\gamma j_a j_b;\gamma j_a' j_b') \ . \tag{8}$$

The expansion of the total scattering wave function in space-fixed eigenfunctions of total angular momentum J with radial product wave functions $f^J(\gamma j_a j_b jl \,|\, R)$, where R is the internuclear distance, yields the set of close-coupled partial-wave scattering equations written in atomic units,

$$\begin{aligned}&\left[\frac{d^2}{dR^2}-\frac{l(l+1)}{R^2}+k_\gamma^2\right]f^J(\gamma j_a j_b jl \,|\, R)\\ &\quad -2\mu\sum_{\substack{\gamma' j_a'\\ j_b' l'}}V^J(\gamma j_a j_b l;\gamma' j_a' j_b' l' \,|\, R)\\ &\qquad \times f^J(\gamma' j_a' j_b j' l' \,|\, R)=0 \ ,\end{aligned} \tag{9}$$

where

$$\begin{aligned}&V^J(\gamma j_a j_b l;\gamma' j_a' j_b' l' \,|\, R)\\ &\quad =\sum_{\Lambda,S} g^{\Lambda S J}(\gamma j_a j_b l;\gamma' j_a' j_b' l')V(\gamma,\gamma';\Lambda S \,|\, R) \ .\end{aligned} \tag{10}$$

In the case considered here, $L_b=L_b'=0$, so that $j_b=s_b$ and $j_b'=s_b'$. The coefficients $g^{\Lambda S J}$ of the diabatic potentials $V(\Lambda S \,|\, R)$ are obtained by expressing the space-fixed functions in terms of the body-fixed functions with which $V(\Lambda S \,|\, R)$ were determined. Standard vector-coupling procedures[9,10] lead to the relation

$$g^{\Lambda S J}(\gamma j_a j_b jl;\gamma' j_a' j_b' j' l')=(-1)^{l_a+l_a'+s_a+s_b+s_a'+s_b'+2S}[S][j_a,j,l,j_a' j',l']^{1/2}\begin{Bmatrix} s_a & s_b & S\\ j & L_a & j_a\end{Bmatrix}\begin{Bmatrix} s_a' & s_b' & S\\ j' & L_a' & j_a'\end{Bmatrix}A_{jj'}^{\Lambda S J} \ , \tag{11}$$

where

$$A_{jj'}^{\Lambda S J}=\sum_{\substack{|m_{l_a}|=\Lambda\\ \Omega,\Sigma}}\begin{bmatrix} L_a & j & S\\ m_{l_a} & -\Omega & \Sigma\end{bmatrix}\begin{bmatrix} L_{a'} & j' & S\\ m_{l_a} & -\Omega & \Sigma\end{bmatrix}\begin{bmatrix} j & J & l\\ \Omega & -\Omega & 0\end{bmatrix}\begin{bmatrix} j' & J & l'\\ \Omega & -\Omega & 0\end{bmatrix} \tag{12}$$

and $[a,b]=(2a+1)(2b+1)$.

The spin-orbit interactions between molecular states separating to different spectral terms are weak and, in addition to the couplings of different (ΛS) diabatic states in the representation (10), we included only the spin-orbit interactions arising from the same spectral term. We assumed that the spin-orbit interactions are independent of internuclear distances and we obtained them directly from the measured fine-structure energy-level separations.[10] As was done in the earlier calculation in which fine-structure was ignored, we neglected rotational couplings between molecular states arising from different spectral terms. The charge transfer of O^{3+} in H at thermal energies is dominated by avoided crossings of states of the same symmetry, but rotational couplings might affect charge transfer in those channels for which

TABLE I. Values of l for a given J in the different channels in the j-j coupling formulation $(\gamma j_a 1/2 jlJ)$. The dashes indicate that there is no value of l corresponding to those values of j and j_a.

Parity	Term	^2p, $2P^0$				$2p3s$, $^3P^0$			$2p3s$, $^1P^0$
	j_a	1/2		3/2		0	1	2	1
	j	0	1	1	2	0	1	2	1
$(-)^J$	l	J	J	J	$J,J\pm2$	J	J	$J,J\pm2$	J
$(-)^{J+1}$	l	–	$J\pm1$	$J\pm1$	$J\pm1$	–	$J\pm1$	$J\pm1$	$J\pm1$

Parity	Term	$2p3p$, ^1P	$2p3p$, ^3D			$2p3p$, ^3s
	j_a	1	1	2	3	1
	j	1	1	2	3	1
$(-)^J$	l	J	$J\pm1$	$J\pm1$	$J\pm1,J\pm3$	$J\pm1$
$(-)^{J+1}$	l	$J\pm1$	J	$J,J\pm2$	$J,J\pm2$	J

the cross sections are small, particularly, capture into the O^{2+}($^1P^0$) and O^{2+}($^3P^0$) states.

We selected those states which give evidence of the existence of avoided crossings.[1] There are 45 scattering channels in Eq. (8) corresponding to capture into the $^1P^0$, ^1P, $^3P^0_{0,1,2}$, $^3D_{1,2,3}$, and ^3S states of O^{2+} by O^{3+}($^2P_{1/2}$) and O^{3+}($^2P_{3/2}$). They divide into two uncoupled blocks of opposite overall parities, one with 22 channels of parity $(-1)^J$ and the other with 23 channels of parity $(-1)^{J+1}$. The permitted values of l for a given J are listed in Table I.

A space-fixed LS-coupled formulation may be obtained from the j-j formulation by expressing the interaction potential matrix (11) in the $|LSjl\rangle$ representation. We apply the projection operator

$$\sum_{j_a} |(L_a s_a)j_a s_b j\rangle\langle(L_a s_a)j_a s_b j|$$

to each side of the interaction matrix (10) with $L_b = L_{b'} = 0$ to obtain

$$\begin{aligned} V^J(\gamma L_a s_a l;\gamma' L_a' s_a l' \mid R) &= \langle L_a(s_a s_b)SjlJ \mid V \mid L_a'(s_a' s_b')S'j'l'J\rangle \\ &= \sum_{j_a j_a'} \langle L_a(s_a s_b)SjM \mid (L_a s_a)j_a s_b jM\rangle\langle(L_a s_a)j_a s_b j \mid V \mid (L_a' s_a')j_a' s_b' j'\rangle \\ &\quad \times\langle(L_a' s_a')j_a' s_b' j'M' \mid L_a(s_a' s_b')Sj'M'\rangle \ . \end{aligned} \tag{13}$$

Now

$$\langle L_a(s_a s_b)SjM \mid (L_a s_a)j_a s_b j'M\rangle = \delta_{jj'}\delta_{MM'}[j_a,S]^{1/2}(-)^{L_a+s_a+s_b+j}\begin{Bmatrix} L_a & s_a & j_a \\ s_b & j & S \end{Bmatrix} , \tag{14}$$

where { } is a 6-j coefficient.[11] Using the orthogonality properties of 6-j coefficients, we may simplify Eq. (13) to the

TABLE II. Values of l for a given J in the LS-coupling formulation $[\gamma L_a(s_a s_b)SjlJ]$. The dashes indicate that there is no value of l corresponding to those values of j and j_a.

Parity	Term	^2p,$^2P^0$				$2p3s$, $^3P^0$			$2p3s$, $^1P^0$
	L_a	1				1			1
	s_a	1/2		1/2		1			0
	s_b	1/2		1/2		0			0
	S	0		1		1			0
	j	1	0	1	2	0	1	2	1
$(-)^J$	1	J	J	J	$J,J\pm2$	J	J	$J,J\pm2$	J
$(-)^{J+1}$	l	$J\pm1$	–	$J\pm1$	$J\pm1$	–	$J\pm1$	$J\pm1$	$J\pm1$

Parity	Term	$2p3p$, ^1P	$2p3p$, ^3D			$2p3p$, ^3s
	L_a	1	2			0
	s_a	0	1			1
	s_b	0	0			0
	S	0	1			0
	j	1	1	2	3	1
$(-)^J$	l	J	$J\pm1$	$J\pm1$	$J\pm1,J\pm3$	$J\pm1$
$(-)^{J+1}$	l	$J\pm1$	J	$J,J\pm2$	$J,J\pm2$	J

TABLE III. Cross sections in units of 10^{-16} cm^2 for $O^{3+}(^2P_{1/2,3/2})+H \rightarrow O^{2+}(^{2s'_a+1}L'_{a j'_a})+H^+$. (Numbers in square brackets denote power of 10.)

E(K)	$^3S_1$	$^3D_3$	$^3D_2$	$^3D_1$	$^1P_1$	$^1P^0_1$	$^3P^0_2$	$3P^0_1$	$3P^0_0$
					$^2P_{1/2}$				
3500	11.6	11.2	7.4	3.6	1.6	1.8[−2]	5.3[−3]	3.1[−3]	8.4[−4]
10 000	11.3	12.0	7.4	3.2	2.0	6.4[−2]	1.0[−2]	4.2[−3]	1.1[−3]
20 000	11.3	12.3	8.0	3.9	2.5	1.7[−1]	1.9[−2]	9.5(−3)	2.5[−3]
					$^2P_{3/2}$				
3500	7.6	13.0	9.1	5.5	2.0	2.7[−2]	5.9[−3]	3.6[−3]	1.5[−3]
10 000	8.7	10.4	8.0	5.7	2.8	7.8[−2]	5.9[−3]	7.3[−3]	2.8[−3]
20 000	9.0	11.1	8.1	5.4	3.5	2.0[−1]	1.7[−2]	1.4[−2]	5.6[−3]

form

$$V^J(\gamma L_a s_a l;\gamma' L'_a s_a l' \mid R) = \sum_{\Lambda,S} g^{\Lambda SJ}(jlL_a, j'l'L'_a) V(\gamma\gamma'\Lambda S \mid R) , \tag{15}$$

where

$$g^{\Lambda SJ}(jlL_a, j'l'L'_a) = (-)^{j+j'}[j,l,j',l']^{1/2} A^{\Lambda SJ}_{jj'} . \tag{16}$$

The cross sections for charge transfer from $(\gamma L_a s_a s_b)$ to $(\gamma' L'_a s'_a s'_b)$ are given by

$$\sigma(\gamma L_a s_a s_b;\gamma' L'_a s'_a s'_b) = \frac{\pi}{(2L_a+1)(2s_a+1)(2s_b+1)k^2_\gamma} \sum_{J,l,l'} (2J+1) \mid T^J(\gamma LSj;\gamma' L'Sj') \mid^2 . \tag{17}$$

The transition matrix is obtained from the asymptotic solutions of the coupled equations derived from the interaction matrix

$$V^J(\gamma L_a s_a l;\gamma' L'_a s'_a l' \mid R) .$$

There are 45 scattering channels, divided as before into two blocks of 22 and 23 channels. The permitted values of l for the two parities are listed in Table II.

The solution of the LS-coupled equations is comparable in difficulty to the solution of the j-j coupled equations, in which proper account may be taken of the fine-structure energy levels. We obtained results with the LS-coupled formulation, nevertheless, in order to compare with the much simpler body-fixed LS-coupled formulation (6), in which no mixing of molecular states with different values of Λ was permitted.

TABLE IV. Cross sections in units of 10^{-16} cm for $O^{3+}(^2P_{3/2})+H \rightarrow O^{3+}(^2P_{1/2})+H$.

E(K)	σ
3500	28.6
10 000	24.7
20 000	23.2

III. RESULTS

The close-coupling equations were solved numerically using the logarithmic derivative method of Johnson.[12] The cross sections were calculated for relative energies E equivalent to temperatures of 3500, 10 000, and 20 000 K. The charge transfer cross sections are shown in Table III, and the direct fine-structure excitation cross sections are shown in Table IV. The different magnitudes of the charge transfer cross sections for capture into the various LS states arise from the relative locations of the avoided crossings of the adiabatic potential-energy curves.[1,2] The cross sections for capture into the fine-structure levels of any LS state exhibit no discernible pattern. The cross-section ratios depend on the initial fine-structure states of O^{3+} and vary with energy. The ratios are not very different from the ratios of the statistical weights, though the cross sections for the highest j level both in the ^3D and ^3P states are less than the statistical weight would suggest.

We compare, in Table V, the cross sections obtained from Eq. (8) at an energy equivalent to 10 000 K with

TABLE V. Charge transfer cross sections for $O^{3+}(^2P)+H \rightarrow O^{2+}(^{2s'_a+1}L'_a)+H$ in units of 10^{-16} cm^2 at an energy corresponding to 10 000 K. (Numbers in square brackets denote power of 10.)

Formulation $^{2s'_a+1}L'_a$	^3S	^3D	^1P	$^1P^0$	$^3P^0$
j-j	10.0	24.1	2.0	2.5[−1]	2.3[−2]
Space-fixed *LS*	10.5	23.1	2.2	6.7[−2]	2.1[−2]
Body-fixed *LS*	10.2	22.0	2.2	7.0[−2]	1.6[−2][a]

[a] The values differ slightly from those of Heil and co-workers (Ref. 1) because of a different choice of asymptotic energy values.

those obtained from the body-fixed *LS* approximation of Heil and co-workers,[1] for which no mixing of different Λ states was allowed, and with the coupled space-fixed *LS* approximation of Eq. (17), in which the mixing of different Λ states of the same asymptotic configuration is included. The agreement between the results of the different calculations is excellent. The differences in the cross sections for capture into the $^1P^0$ and $^3P^0$ terms arise because small cross sections are more sensitive to the fine-structure-level splittings neglected in both of the *LS* approximations and to the Λ couplings neglected in the body-fixed approximation.

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