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Fine structure transitions of C^+ in collisions with H_2

Shih-I Chu^{*†} and A. Dalgarno

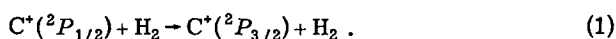
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Close-coupling calculations are described of the cross sections for the fine-structure excitation of C^+ in collisions with molecular hydrogen for energies up to 0.2 eV. A table is presented of the cooling rate coefficients for temperatures between 10–1000 °K.

I. INTRODUCTION

The excitation of the $^2P_{3/2}$ level of C^+ by collisions of hydrogen atoms, followed by the emission of a photon at 156 μ , is the major cooling mechanism in cold diffuse interstellar clouds of atomic hydrogen, and calculations have been made of its efficiency.¹ In many of the clouds observed using the ultraviolet spectrophotometer on the Copernicus satellite, the hydrogen is mainly in molecular form² and the major cooling mechanism is



For its efficiency, there is available only the estimate of Dalgarno and McCray³ that it may be approximately 25% of that of the reaction with atomic hydrogen.

The theory of fine-structure transitions in collisions with atoms has been discussed recently by Reid and Dalgarno,⁴ Reid,⁵ Mies,⁶ and Preston, Sloane, and Miller.⁷ In this paper, we extend the approach followed by Mies⁶ to collisions with hydrogen molecules. Related studies have been reported recently by Tully⁸ and by Zimmerman and George.⁹

II. INTERACTION POTENTIALS

We regard the hydrogen molecule as a rigid rotator of mass M_{H_2} and moment of inertia I with Hamiltonian H_r . If \hat{s} specifies the orientation of the internuclear axis with respect to axes fixed in space, the eigenfunctions $Y_{j_b m_{j_b}}(\hat{s})$ of H_r satisfy the equation

$$H_r Y_{j_b m_{j_b}}(\hat{s}) = \frac{\hbar^2}{2I} j_b(j_b + 1) Y_{j_b m_{j_b}}(\hat{s}); \quad (2)$$

$Y_{j_b m_{j_b}}$ is a spherical harmonic.

The Hamiltonian of the carbon ion C^+ can be written

$$H_c + V_{LS}(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^5 \nabla_{\mathbf{r}_i}^2 + \sum_{i>j}^5 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - 6 \sum_{i=1}^5 \frac{1}{r_i} + V_{LS}(\mathbf{r}), \quad (3)$$

where \mathbf{r}_i is the position vector of the i th electron measured from the C^+ nucleus and $V_{LS}(\mathbf{r})$ is the spin-orbit interaction which we write in the form

$$V_{LS}(\mathbf{r}) = \sum_i f_i(\mathbf{r}_i) \mathbf{l}_i \cdot \mathbf{s}_i, \quad (4)$$

\mathbf{l}_i and \mathbf{s}_i being, respectively, the orbital and spin angular momentum of the i th electron.

The electronic Hamiltonian $H_c(\mathbf{r})$ commutes with the electron orbital angular momentum L^2 and the projection, L_z , of L on a space-fixed axis, and with the spin

angular momentum S^2 and the projection, S_z , of S on a space-fixed axis. Let $\phi(nL S m_L m_S)$ be the eigenfunction corresponding to the specified quantum numbers, $nL S m_L m_S$, labelling the eigenvalue $\epsilon(n, L, S)$. The eigenfunction corresponding to the total angular momentum $\mathbf{j}_a = \mathbf{L} + \mathbf{S}$ can be written as the sum

$$\Phi(nL S j_a m_{j_a}) = \sum_{m_L, m_S} C(L, S, j_a; m_L m_S m_{j_a}) \phi(nL S m_L m_S), \quad (5)$$

where C is a Clebsch-Gordan coefficient. Suppose Δ is the fine-structure splitting of an isolated C^+ ion in the ground 2P state and write V_{LS} in the form

$$V_{LS} = \frac{2}{3} \Delta \mathbf{L} \cdot \mathbf{S}. \quad (6)$$

Then,

$$\langle j'_a m_{j'_a} | H_c + V_{LS} | j_a m_{j_a} \rangle = \frac{1}{3} \Delta [j_a(j_a + 1) - L(L + 1) - J(J + 1)] \delta_{j'_a j_a} \delta_{m_{j'_a} m_{j_a}}, \quad (7)$$

where we have chosen an energy origin such that $\epsilon(01\frac{1}{2}) = 0$.

The Hamiltonian for the interacting $C^+ - H_2$ system is

$$\mathcal{H} = -\nabla_{\mathbf{R}}^2 / 2\mu + H_r + H_c(\mathbf{r}) + H_{ab} + V_{LS}(\mathbf{r}, \mathbf{R}), \quad (8)$$

where μ is the reduced mass

$$\mu = M_{H_2} M_{C^+} / (M_{H_2} + M_{C^+}), \quad (9)$$

$$H_{ab} = H_c(\mathbf{r}) + V(\mathbf{r}, \mathbf{R}), \quad (10)$$

and $V(\mathbf{r}, \mathbf{R})$ is the electrostatic interaction between C^+ and H_2 . The electronic term H_{ab} is the adiabatic Hamiltonian for the CH_2^+ complex in the Born-Oppenheimer approximation. For a linear approach in which C^+ approaches H_2 along its internuclear axis, the symmetry is $C_{\infty v}$ and there are two adiabatic molecular states, one of $^2\Pi$ and one of $^2\Sigma$ symmetry. Both dissociate asymptotically to a product of the states $C^+(^2P)$ and $H_2(X^1\Sigma_g^+)$. For perpendicular approach, the symmetry is C_{2v} and there are three adiabatic molecular states, 2A_1 , 2B_1 , and 2B_2 .

Simultaneous excitation of fine-structure and molecular rotation is improbable, and in our calculations of the fine-structure cross sections we supposed that the molecule remains in the lowest rotational level $j_b = 0$ during the collisions. The cross sections are controlled mainly by the interactions at separations of C^+ and H_2 near 3 Å, where the splitting between the $^2\Sigma$ and $^2\Pi$ levels is comparable to the spin-orbit interaction. At separations larger than about 3 Å, the orientation of lowest energy is that occurring with $C_{\infty v}$ symmetry, and we assumed

that the $C_{\infty V}$ interactions are responsible for the fine-structure excitation.

To describe the adiabatic molecular eigenfunctions, it is convenient to employ molecular-fixed coordinates. We rotate the space-fixed axes through the Eulerian angle $(\phi, \theta, 0)$, where ϕ and θ are the polar coordinates of $\hat{\mathbf{R}}$. Then \mathcal{H} becomes

$$\mathcal{H}(\mathbf{r}, R, \theta, \phi) = -\frac{1}{2\mu} \left(\frac{d^2}{dR^2} + \frac{2}{R} \frac{d}{dR} \right) + \frac{\mathbf{L}_R^2(\theta, \phi)}{2\mu R^2} + H_r + H_{ab} + V_{LS}(\mathbf{r}, R), \quad (11)$$

where \mathbf{L}_R is the nuclear angular momentum in body-fixed coordinates,

$$\mathbf{L}_R \equiv i\mathbf{R} \times \nabla_{\mathbf{R}} \equiv \mathbf{J} - \mathbf{j}_a = \mathbf{J} - \mathbf{L} - \mathbf{S}, \quad (12)$$

\mathbf{J} being the total angular momentum of the C⁺-H-H complex. The adiabatic molecular eigenfunctions, $\Psi_{\Lambda m_S}^{nLS}(R)$, satisfy the equation

$$H_{ab} \Psi_{\Lambda m_S}^{nLS}(R) = E_{\Lambda}^{nLS}(R) \Psi_{\Lambda m_S}^{nLS}, \quad (13)$$

where Λ is the quantized molecule-fixed projection of \mathbf{L} along the intermolecular axis R . Thus, the eigenvalues for the molecular complex which dissociates into C⁺(²P) and H₂(¹Σ_g⁺, $j_b=0$) are given by

$$E_{1\Lambda}(R) \equiv E_{1\Lambda}^{011/2}(R) = \langle \Psi_{\Lambda m_S}^{011/2}(R) | V(\mathbf{r}, R) | \Psi_{\Lambda m_S}^{011/2}(R) \rangle, \quad (14)$$

which tends to zero at infinite separation. At finite R , the asymptotically degenerate Λ states are split by the interaction of C⁺ and H₂. The ground state of C⁺(²P) has $L=1$, Λ can take the values 0, ±1, and C⁺(²P) correlates with the lowest ²Σ ($\Lambda=0$) and the doubly-degenerate ²Π ($\Lambda=\pm 1$) states of C⁺-H-H.

The potential curves ²Σ and ²Π of the linear C⁺-H-H complex at short and intermediate values of R have been calculated recently by Liskow, Bender, and Schaefer.¹⁰ The long-range part of molecular potentials can be evaluated by perturbation theory. We regard the C⁺ ion as a core of charge +2 with an active 2p electron with coordinate \mathbf{r} . The resulting interaction, $V^{\text{eff}}(\mathbf{r}, R)$, with H₂ depends only on $\mathbf{r} \equiv r \hat{\mathbf{r}}$, and \mathbf{R} . It can be expanded in the form

$$V^{\text{eff}}(\mathbf{r}, R) = \sum_{\mu=0}^{\infty} v_{\mu}(r, R) P_{\mu}(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}), \quad (15)$$

in which case

$$E_{1\Lambda}(R) = \sum_{\mu} C(1\mu 1; \Lambda 0 \Lambda) C(1\mu 1; 000) \hat{v}_{\mu}(R), \quad (16)$$

where $\hat{v}_{\mu}(R)$ is the expectation value of $v_{\mu}(r, R)$ for the 2p orbital. $C(1\mu 1; 000)$ is zero unless μ is an even integer. If we retain only the first two leading nonvanishing terms in Eq. (16), we have

$$\begin{aligned} E_0(R) &\equiv E(^2\Sigma | R) = \hat{v}_0(R) + 2/5 \hat{v}_2(R), \\ E_1(R) &\equiv E(^2\Pi | R) = \hat{v}_0(R) - 1/5 \hat{v}_2(R). \end{aligned} \quad (17)$$

Using the results of Appendix A, we obtain for \hat{v}_0 and \hat{v}_2 ,

$$\begin{aligned} \hat{v}_0(R) &\sim \frac{e\Theta_2}{R^3} - \frac{e^2\alpha_{2\parallel}}{2R^4}, \\ \hat{v}_2(R) &\sim \frac{6e\Theta_2\langle r^2 \rangle}{R^5} + \frac{1}{3} e^2 [5\alpha_{2\parallel} + \alpha_{2\perp}] \frac{\langle r^2 \rangle}{R^6}, \end{aligned} \quad (18)$$

where Θ_2 , $\alpha_{2\parallel}$, and $\alpha_{2\perp}$ are, respectively, the permanent quadrupole moment, and the parallel and perpendicular polarizabilities, and $\langle r^2 \rangle$ is the expectation value of r^2 for C⁺.

It is convenient at this point to introduce molecular complex wavefunctions $\Psi_{j\Omega}(R)$ which become diagonal in both j^2 and j_z at infinite separation⁶

$$\Psi_{j\Omega}(R) \underset{R \rightarrow \infty}{\sim} \Phi_{j\Omega}, \quad (19)$$

where $\Phi_{j\Omega}$ are atomic states which diagonalize the spin-orbit operator and Ω is the projection of $\mathbf{j} = \mathbf{L} + \mathbf{S}$ along \mathbf{R} . The wavefunctions $\Psi_{j\Omega}(R)$ can be constructed by taking linear combinations of the eigenfunctions of H_{ab} according to

$$\Psi_{j\Omega}(R) = \sum_{\Lambda, m_S} C(L, S, j; \Lambda, m_S, \Omega) \Psi_{\Lambda m_S}(R), \quad (20)$$

where $\Psi_{\Lambda m_S}(R) \equiv \Psi_{\Lambda m_S}^{011/2}(R)$. The spin-orbit operator $V_{LS}(\mathbf{r}, R)$ in the representation of $\Psi_{j\Omega}(R)$ can be approximately evaluated by

$$\langle \Psi_{j\Omega}(R) | V_{LS}(\mathbf{r}, R) | \Psi_{j'\Omega}(R) \rangle \approx \langle \Phi_{j\Omega} | V_{LS}(\mathbf{r}) | \Phi_{j'\Omega} \rangle, \quad (21)$$

in which case the expectation values of V_{LS} become independent of R . The matrix elements in (21) are given by expressions similar to Eq. (7). The matrix elements of the molecular states in the j, Ω representation are given by

$$\langle \Psi_{j\Omega}(R) | H_{ab} + V_{LS} | \Psi_{j'\Omega}(R) \rangle = \delta_{j'\Omega} \{ (E_1(R) + \epsilon_j) \delta_{jj'} + (E_0(R) - E_1(R)) \cdot C(1\frac{1}{2} j | 0 \Omega \Omega) \cdot C(1\frac{1}{2} j' | 0 \Omega \Omega) \}, \quad (22)$$

where $\epsilon_{1/2} = -\frac{2}{3}\Delta$, $\epsilon_{3/2} = \frac{1}{3}\Delta$, and $E_0(R) \equiv E(^2\Sigma | R)$, and $E_1(R) \equiv E(^2\Pi | R)$. Explicitly,

$$\begin{aligned} \langle \Psi_{3/2, \pm 3/2}(R) | H_{ab} + V_{LS} | \Psi_{3/2, \pm 3/2}(R) \rangle &= E_1 + \frac{1}{3}\Delta, \\ \langle \Psi_{3/2, \pm 1/2}(R) | H_{ab} + V_{LS} | \Psi_{3/2, \pm 1/2}(R) \rangle &= \frac{1}{3}(2E_0 + E_1) + \frac{1}{3}\Delta, \\ \langle \Psi_{1/2, \pm 1/2}(R) | H_{ab} + V_{LS} | \Psi_{1/2, \pm 1/2}(R) \rangle &= \frac{1}{3}(E_0 + 2E_1) - \frac{2}{3}\Delta, \\ \langle \Psi_{1/2, \pm 1/2}(R) | H_{ab} + V_{LS} | \Psi_{3/2, \pm 1/2}(R) \rangle &= \pm \frac{1}{3}\sqrt{2} (E_1 - E_0). \end{aligned} \quad (23)$$

Thus, the molecular eigenfunctions $\Psi_{j\Omega}(R)$ yield asymptotically accurate atomic eigenvalues and eigenfunctions.

At finite R , $\Psi_{j\Omega}(R)$ no longer diagonalize H_{ab} , as is evidenced by the off-diagonal elements in (23). The off-diagonal terms are responsible for the $j=1/2 \rightleftharpoons j'=3/2$ coupling in the scattering theory.

III. SCATTERING THEORY

The scattering theory we adopt to describe the fine-structure transition

$$C^+(^2P_j) + H_2(X^1\Sigma_g^+, j_b=0) = C^+(^2P_j) + H_2(X^1\Sigma_g^+, j_b'=0) \quad (24)$$

is a close-coupling formulation. The scattering event is characterized by the asymptotic behavior of the total wavefunction $\Psi(E)$, which is a particular solution of the Schrödinger equation at total energy E :

$$\left[\mathcal{H} - E \right] \Psi(E) = \left[-\frac{1}{2\mu} \left(\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + \frac{L_R^2}{2\mu R^2} + (H_c(\mathbf{r}) + V(\mathbf{r}, \mathbf{R}) + V_{LS}(\mathbf{r}, \mathbf{R})) \right] \Psi(E) = 0. \quad (25)$$

The asymptotic wavefunctions can be represented by

$$\Psi(E) \underset{R \rightarrow \infty}{\sim} \sum_{\alpha} G_{\alpha}(R) |\alpha\rangle, \quad (26)$$

where $|\alpha\rangle$ are the channel states and are eigenfunctions of $L_R^2/2\mu R^2$ and of $(H_c + V_{LS})$ with eigenvalues ϵ_{α} ; the radial functions $G_{\alpha}(R)$ satisfy

$$\left[-\frac{1}{2\mu} \left(\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + \epsilon_{\alpha} - E \right] G_{\alpha}(R) \underset{R \rightarrow \infty}{\sim} 0. \quad (27)$$

We construct molecular channel states⁶ with the eigenfunctions $\Psi_{j\Omega}(R)$ of $(H_c + V_{LS} + V)$ in molecule-fixed coordinates. Because of the $C_{\infty v}$ symmetry of the collision system, it is expedient to expand the angular dependence $\hat{R} = (\theta, \phi)$ in terms of normalized symmetric-top wavefunctions:

$$\Omega_{M,\Omega}^J(\theta, \phi) = \sqrt{\frac{2J+1}{4\pi}} D_{M,\Omega}^{J*}(\phi, \theta, 0), \quad (28)$$

where M is the space-fixed projection of J . The total angular momentum states are then simply constructed as products of $\Omega_{M,\Omega}^J$ and $\Psi_{j\Omega}(R)$. This procedure yields⁶ the molecular channel states $Z_{ji}^{JM}(\mathbf{r}, \mathbf{R})$:

$$Z_{ji}^{JM}(\mathbf{r}, \mathbf{R}) = \sum_{\Omega} (-1)^{J+\Omega} C(J, j, l | -\Omega, \Omega, 0) \cdot \Omega_{M,\Omega}^J(\hat{R}) \Psi_{j\Omega}(R). \quad (29)$$

The Clebsch-Gordan coefficients in Eq. (29) show that for a given J and M , there are at most six channel states if C⁺ is in either of the ground ²P states. However, channel states with different parity are uncoupled, and the channel states can be grouped according to their parities. The result is given in Table I.

The total wavefunction can now be expanded in terms of Z_{ji}^{JM} ,

$$\Psi_{ji}^{JM}(E) = \sum_{j', i'} G_{j', i'}^{J, M, E}(R) Z_{j', i'}^{JM}(\mathbf{r}, \mathbf{R}). \quad (30)$$

Substituting (30) into (25), we obtain the set of coupled equations for $G(R)$:

$$\sum_{j', i'} \langle Z_{ji}^{JM}(\mathbf{r}, \mathbf{R}) | \mathcal{H} - E | Z_{j', i'}^{JM}(\mathbf{r}, \mathbf{R}) \rangle G_{j', i'}^{J, M, E}(R) = 0. \quad (31)$$

TABLE I. Channel states for a particular J .

Parity = $(-)^{J+1/2}$	Parity = $(-)^{J-1/2}$
$j=3/2, l=J+3/2$	$j=3/2, l=J-3/2$
$j=3/2, l=J-1/2$	$j=3/2, l=J+1/2$
$j=1/2, l=J-1/2$	$j=1/2, l=J+1/2$

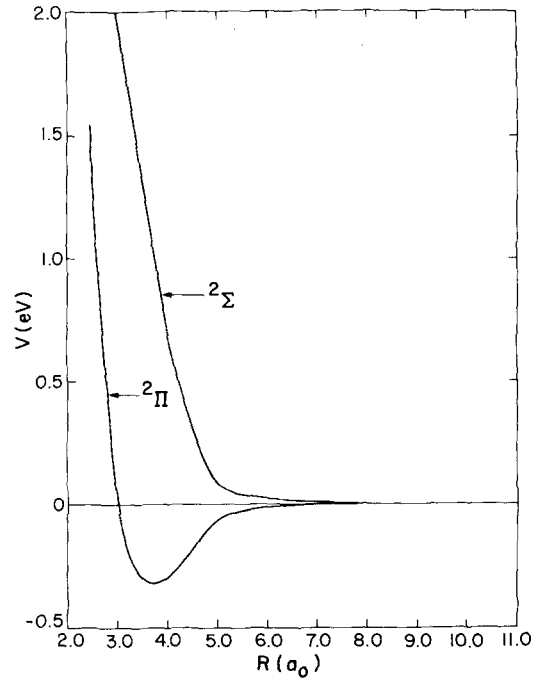


FIG. 1. Molecular potentials for the linear C⁺...H-H complex.

If we include only the six open-channel states tabulated in Table I, Eq. (31) generates two sets of *three* coupled equations for each J, M .

The evaluation of the matrix elements $\langle Z | \mathcal{H} - E | Z \rangle$ has been discussed by Mies.⁶ If we neglect the angular and radial Born-Oppenheimer matrix elements, the equations reduce to

$$\left[\left(-\frac{\hbar^2}{2\mu} \frac{\partial^2 R}{R \partial R^2} - E \right) \mathbf{1} + \mathbf{U}^J(R) \right] \mathbf{G}(R) = 0, \quad (32)$$

where $\mathbf{G} = \{G_{ji, j', i'}(R)\}$ and $\mathbf{1} = \{\delta_{jj'}, \delta_{ii'}\}$, \mathbf{G} and $\mathbf{1}$ being column vectors, and the interaction matrix $\mathbf{U}^J(R)$ is de-

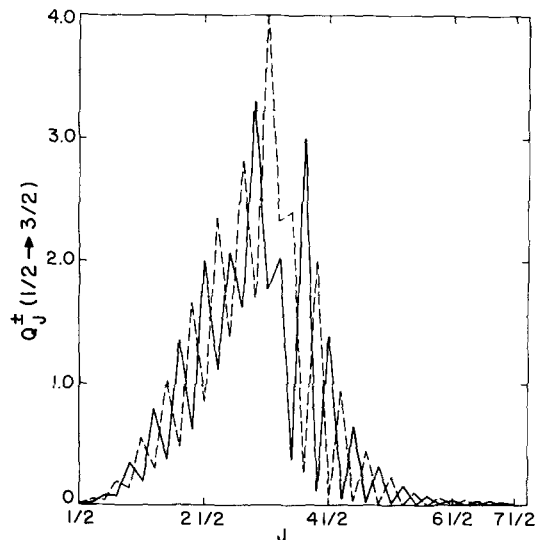


FIG. 2. Oscillatory behavior of the partial cross sections Q_J^+ for fine structure transition C⁺(²P_{1/2} → ²P_{3/2}) at $E_{tot} = 0.0275$ eV. The solid line is Q_J^+ and the dashed line is Q_J^- .

finned such that

$$U_{j,l;j',l'}^J(R) = \delta_{jj'} \delta_{ll'} [\epsilon_j + E(^2\Pi | R) + l(l+1)/2\mu R^2] + C_{j,l;j',l'}^J [E(^2\Sigma | R) - E(^2\Pi | R)], \quad (33)$$

with

$$C_{j,l;j',l'}^J = \sum_{\Omega} (-1)^{j'-j} C(J, j, l | -\Omega, \Omega, 0) \cdot C(J, j', l' | -\Omega, \Omega, 0) C(1, \frac{1}{2}, j | 0, \Omega, \Omega) \cdot C(1, \frac{1}{2}, j' | 0, \Omega, \Omega). \quad (34)$$

The atomic eigenvalues ϵ_j are $\epsilon_{1/2} = -\frac{2}{3}\Delta$ and $\epsilon_{3/2} = \frac{1}{3}\Delta$.

Equation (32) can be further simplified with the substitution

$$\mathbf{F}(R) = R \cdot \mathbf{G}(R)$$

such that

$$\left[\left(\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + E \right) \mathbf{1} - \mathbf{U}^J(R) \right] \mathbf{F}(R) = 0. \quad (35)$$

This set of coupled differential equations can be solved by standard procedures. The boundary conditions are

$$F_{j,l;j',l'}^J(R=0) = 0, \quad (36a)$$

$$F_{j,l;j',l'}^J(R) \underset{R \rightarrow \infty}{\sim} \delta_{jj'} \delta_{ll'} \left\{ -2i \sin(k_j R - \frac{1}{2} l \pi) \right\} + \sqrt{\frac{k_j}{k_{j'}}} T^J(j, l; j' l') \exp \left\{ i \left(k_j R - \frac{l' \pi}{2} \right) \right\}, \quad (36b)$$

which defines the T -matrix which is symmetric in (j, l) and (j', l') .

The total cross section for the $j \rightarrow j'$ transition, after a transformation from the body frame to the laboratory frame, and a summation over $m_{j'}$ and an average over m_j have been taken, is given by

$$\sigma(j \rightarrow j') = \frac{\pi}{(2j+1)k_j^2} \sum_J \sum_l \sum_{l'} (2J+1) |T^J(jl; j'l')|^2 = \sum_J \{ Q_J^+(j \rightarrow j') + Q_J^-(j \rightarrow j') \}, \quad (37)$$

where Q_J^\pm are the partial cross sections for even (+) and odd (-) parity at a given total angular momentum J (cf. Table I).

TABLE II. Spin-change cross sections (in units of a_0^2) for $C^+(P_j) + H_2 \rightarrow C^+(P_{j'}) + H_2$.

E (eV)	$\sigma(\frac{1}{2} \rightarrow \frac{3}{2})$	$\sigma(\frac{3}{2} \rightarrow \frac{1}{2})$
0.01	5.1	5.2
0.0125	12.7	11.4
0.0150	16.4	13.4
0.0175	23.4	17.9
0.0275	51.5	33.9
0.035	68.8	42.8
0.045	82.8	49.1
0.075	94.0	52.2
0.10	96.9	52.4
0.20	77.7	40.4

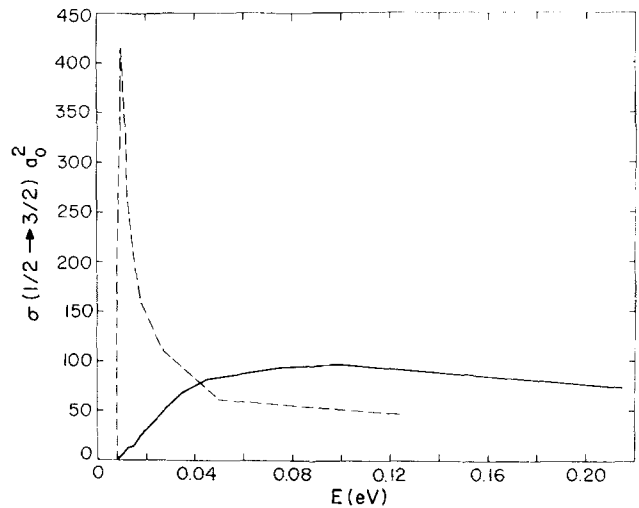


FIG. 3. $\sigma(1/2 \rightarrow 3/2)$ as a function of barycentric energy for $C^+ + H$ and $C^+ + H_2$ collisions. The solid line refers to $(C^+ + H_2)$ collisions and the dashed line to $(C^+ + H)$ collisions.

IV. RESULTS AND DISCUSSIONS

The $^2\Sigma$ and $^2\Pi$ potential curves for the linear $C^+ - H - H$ complex [$R(H-H) = 1.4 a_0$] have been calculated by Lisikow, Bender, and Schaefer¹⁰ out to $R = 4 a_0$. We joined these curves smoothly to an effective long-range interaction at $R \approx 5 a_0$. The resulting curves are shown in Fig. 1.

The quantity

$$\langle r^2 \rangle = \langle \Psi_{C^+(2p)} | r^2 | \Psi_{C^+(2p)} \rangle = 2.689 a_0^2,$$

which appears in the long-range potentials, was computed by Weisheit and Lane¹ from Hartree-Fock atomic wavefunctions.¹¹

The integration of the coupled equations (35) was performed numerically using the Numerov algorithm,¹² and cross sections were calculated from Eq. (37). Figure 2 depicts the partial cross sections Q_J^\pm for inelastic ($\frac{1}{2} \rightarrow \frac{3}{2}$) scattering at $E = 0.0275$ eV. The oscillatory behavior is typical of the $C^+ + H_2$ inelastic cross sections at all energies concerned. The cross sections Q_J^+ and Q_J^- show similar oscillatory structures.

Table II gives the total inelastic cross sections, $\sigma(\frac{1}{2} \rightarrow \frac{3}{2})$ and $\sigma(\frac{3}{2} \rightarrow \frac{1}{2})$, for several barycentric energies. For $E > 0.045$ eV, the tabulated cross sections are subject to some uncertainty because of the opening of rotational excitation channels of H_2 . The table shows that $\sigma_{j \rightarrow j'}(E)$ is a smooth function of E . The cross section is zero at threshold, rising with increasing energy to a maximum at approximately 0.1 eV and then decreasing.

It is of interest to compare the cross sections with those for $C^+ + H$ collisions.¹ The comparison is sketched in Fig. 3. The inelastic cross sections for $C^+ + H_2$ are about an order of magnitude smaller than those for $C^+ + H$ at lower energies, though the elastic cross sections $\sigma(\frac{1}{2} \rightarrow \frac{1}{2})$ for $C^+ + H_2$ are substantially larger than for $C^+ + H$. For $C^+ + H$, $\sigma(\frac{1}{2} \rightarrow \frac{3}{2})$ reaches a maximum at E near 0.01 eV, whereas for $C^+ + H_2$, the maximum occurs

TABLE III. Fine structure cooling rate coefficient $L(T)$.

$T^\circ\text{K}$	$L(T) \times 10^{24} (\text{erg} \cdot \text{cm}^3 \text{sec}^{-1})$
10	1.08×10^{-5}
20	3.44×10^{-3}
30	2.48×10^{-2}
40	7.08×10^{-2}
50	0.138
60	0.222
70	0.319
80	0.424
100	0.650
150	1.24
200	1.78
300	2.69
400	3.39
600	4.37
800	5.06
1000	5.60

at $E \sim 0.1$ eV. That the C⁺ + H₂ system has larger elastic and smaller inelastic cross sections than has the C⁺ + H system may be attributed to the relative magnitude of the leading spherically symmetric long-range interactions which decrease as R^{-3} for the C⁺ + H₂ system, and as R^{-4} for the C⁺ + H system.

The associated cooling rate coefficients for C⁺(²P_{3/2}) at a kinetic temperature $T^\circ\text{K}$,

$$L(T) = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \frac{1}{(kT)^2} \Delta E(j=3/2-1/2) \times \int_0^\infty \sigma(3/2-1/2|E) E \exp(-E/kT) dE,$$

are important in controlling the temperature of interstellar clouds. The results are presented in Table III for the temperature range 10–1000 °K.

Our treatment does not make proper allowance for the averaging over orientation that occurs, averaging that would decrease the influence of the long-range quadrupole–quadrupole interaction for collisions with molecules in the lowest rotational state $j=0$. However, the quadrupole–quadrupole terms provide only a small contribution to the interactions at the separations that control the excitation process, and the cross sections should not be very different for excitation by $j=0$ and $j=1$

$$V_P^{\text{eff}} \equiv -\frac{1}{2} \alpha_{\alpha\beta} E_\alpha E_\beta = \left\{ [\alpha_{211} R^2 + r^2 (\frac{2}{3} \alpha_{211} + \frac{1}{3} \alpha_{211})] - (2Rr \alpha_{211}) P_1(\cos\theta) + [\frac{2}{3} r^2 (\alpha_{211} - \alpha_{211})] P_2(\cos\theta) \right\} / R^{16} - \frac{2e^2 \alpha_{211}}{R^4} + \frac{[(2e^2 \alpha_{211} / R^2)(R - r P_1(\cos\theta))]}{R^3}, \quad (\text{A5})$$

and

$$V_Q^{\text{eff}} \equiv -\frac{1}{3} \Theta_{\alpha\beta} E_{\alpha\beta} = e \Theta_2 R^2 / R'^5 - (2e \Theta_2 R r / R'^5) \times P_1(\cos\theta) + (e \Theta_2 r^2 / R'^5) P_2(\cos\theta). \quad (\text{A6})$$

We wish to expand V^{eff} in terms of Legendre polynomials,

molecules. Certainly within the accuracy with which the interaction potential is known, the cross sections may be taken as equal.

APPENDIX A: EFFECTIVE LONG-RANGE INTERACTION OF C⁺ AND H₂

We treat the C⁺ ion as a core of charge +2, consisting of the carbon nucleus and the four electrons in the 1s and 2s shells, and a 2p electron with coordinate r . The long-range interaction which is responsible for scattering can be rewritten as

$$V^{\text{eff}} \sim -\frac{1}{2} \alpha_{\alpha\beta} E_\alpha E_\beta - \frac{1}{3} \Theta_{\alpha\beta} E_{\alpha\beta}, \quad (\text{A1})$$

where $\alpha_{\alpha\beta}$ and $\Theta_{\alpha\beta}$ are, respectively, the polarizability and quadrupole moment tensors of the H₂ molecule, and E_α and $E_{\alpha\beta}$ are, respectively, the electric field and the field gradient at the center of mass of the H₂ molecule produced by the C⁺⁺ ion core and the 2p electron.

The geometry and the coordinate system for the colliding system are sketched in Fig. 4. The polarizability and quadrupole moment tensor components of H₂ are

$$\alpha_{\alpha\beta} = \frac{1}{3} (\alpha_{211} + 2\alpha_{21}) \delta_{\alpha\beta} + \frac{1}{3} (\alpha_{211} - \alpha_{21}) (3l_\alpha l_\beta - \delta_{\alpha\beta}),$$

and

$$\Theta_{\alpha\beta} = \frac{1}{2} \Theta_2 (3l_\alpha l_\beta - \delta_{\alpha\beta}),$$

where α_{211} and α_{21} are the parallel and perpendicular components of polarizability of H₂ and Θ_2 is the permanent quadrupole moment. The quantities l_α ($\alpha=x, y, z$) are the direction cosines of the H–H internuclear axis. The long-range interaction (A1) in the linear geometry reduces to

$$V^{\text{eff}} = -\frac{1}{2} (\alpha_{xx} E_x^2 + \alpha_{yy} E_y^2 + \alpha_{zz} E_z^2) - \frac{1}{3} (\Theta_{xx} E_{xx} + \Theta_{yy} E_{yy} + \Theta_{zz} E_{zz}). \quad (\text{A2})$$

Now the electric field \mathbf{E} at the center of mass of H₂ is

$$\mathbf{E} = -\frac{e\hat{\mathbf{R}}'}{R'^2} + \frac{2e\hat{\mathbf{R}}}{R^2}, \quad (\text{A3})$$

where $\hat{\mathbf{R}}$ is the unit vector from C⁺⁺ to the center of mass of H₂, and $\hat{\mathbf{R}}'$ is the unit vector from the 2p electron.

Equation (A2) can now be written in terms of R , R' , r and the angle $\theta [= \cos^{-1}(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}})]$:

$$V^{\text{eff}} = V_P^{\text{eff}} + V_Q^{\text{eff}}, \quad (\text{A4})$$

where

$$V^{\text{eff}} = \sum_\lambda v_\lambda(R, r) P_\lambda(\cos\theta). \quad (\text{A7})$$

To do so, we must obtain R'^{-n} in terms of R , r , and $\cos\theta$. Note that

$$R'^2 = R^2 + r^2 - 2Rr \cos\theta, \quad (\text{A8})$$

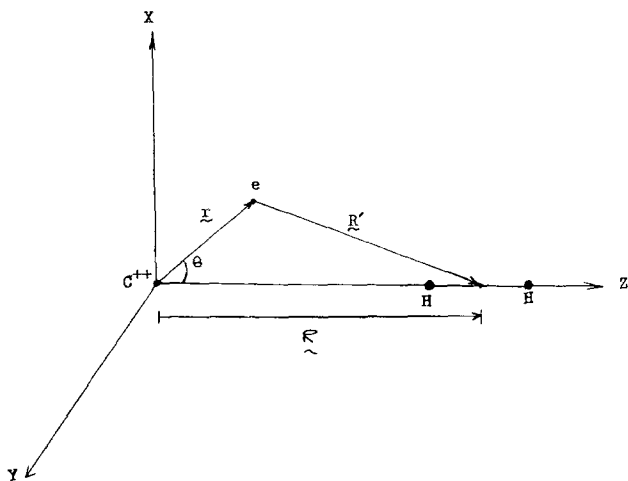


FIG. 4. The geometry and coordinate system for calculating the C⁺ + H₂ effective long-range interaction.

and for $r < R$

$$R'^{-1} = R^{-1} \sum_{k=0}^{\infty} \left(\frac{r}{R}\right)^k P_k(\cos\theta). \quad (\text{A9})$$

$$R'^{-(2n+3)} = \frac{2^n n!}{(2n+1)!} \frac{1}{(R^2 - r^2)^{2n+1}} \times \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \binom{k+n+\frac{1}{2}}{n-m} \binom{k-n+m-\frac{1}{2}}{m} \times (2k+1) \left(\frac{r}{R}\right)^{2m+k} R^{2n-1} P_k(\cos\theta). \quad (\text{A13})$$

Substituting Eqs. (A12)–(A13) into (A5) and (A6) and using

$$P_{l_1}(x) P_{l_2}(x) = \sum_l C(l_1 l_2 l; 000)^2 P_l(x), \quad (\text{A14})$$

we arrive at

$$V_p^{\text{eff}} = -\frac{1}{2} e^2 \left\{ \alpha_{20} / R^4 + \left(\frac{2}{3} \alpha_{20} + \frac{1}{3} \alpha_{21}\right) (r^2 / R^6) + \dots \right\} P_0(\cos\theta) - \frac{1}{2} e^2 \left\{ -4 \alpha_{20} (r / R^5) + \frac{1}{5} (-6 \alpha_{20} + 12 \alpha_{21}) (r^3 / R^7) + \dots \right\} P_1(\cos\theta) - \frac{1}{2} e^2 \left\{ \left(-\frac{10}{3} \alpha_{20} - \frac{2}{3} \alpha_{21}\right) r^2 / R^6 + \left(\frac{176}{21} \alpha_{20} + \frac{160}{21} \alpha_{21}\right) (r^4 / R^8) + \dots \right\} P_2(\cos\theta), \quad (\text{A15})$$

and

$$V_0^{\text{eff}} = e\Theta_2 \left[1/R^3 - \frac{11}{3} (r^2 / R^5) + \dots \right] P_0(\cos\theta) + e\Theta_2 \left[3(r / R^4) - \frac{11}{3} (r^3 / R^6) + \dots \right] \times P_1(\cos\theta) + e\Theta_2 \left[6(r^2 / R^5) + \dots \right] P_2(\cos\theta) + \dots. \quad (\text{A16})$$

In deriving (A15) and (A16), we have implicitly assumed that $\bar{R}^2 - r^2 \approx R^2$, a relation valid for large R , and only terms up to P_2 have been retained.

Thus, the effective long-range interaction can be expanded in the form (A17):

$$V^{\text{eff}} = \sum_{\lambda} v_{\lambda}(R, r) P_{\lambda}(\cos\theta), \quad (\text{A17})$$

with the first three $v_{\lambda}(R, r)$ given by

$$v_0 = e\Theta_2 / R^3 - e^2 \alpha_{20} / 2R^4 + \dots, \quad (\text{A17}')$$

$$v_1 = 3e\Theta_2 r / R^4 + 2e^2 \alpha_{20} r / R^5 + \dots, \quad (\text{A17}''')$$

$$v_2 = 6e\Theta_2 r^2 / R^5 + \frac{1}{3} e^2 [5\alpha_{20} + \alpha_{21}] (r^2 / R^6) + \dots. \quad (\text{A17}''')$$

For each v_{λ} , only the first two leading terms were used in the scattering calculation.

The generating function R'^{-2} is easily obtained. Let $t = (r^2 + R^2) / 2Rr$ and $u = \cos\theta$ so that $R'^{-2} = [2Rr(t - u)]^{-1}$. Write $R'^{-2} = \sum_{k=0}^{\infty} (2k+1) A_k(t) P_k(u)$. The expansion coefficients $A_k(t)$ are given by

$$A_k(t) = \frac{1}{4Rr} \int_{-1}^{+1} \frac{P_k(u) du}{t - u} \equiv \frac{1}{2Rr} Q_k(t), \quad (\text{A10})$$

where $Q_k(t)$ is the Legendre function of the second kind. Then

$$R'^{-2} = \sum_{k=0}^{\infty} (2k+1) (2Rr)^{-1} Q_k(t) P_k(\cos\theta). \quad (\text{A11})$$

This relation can be generalized to higher even powers¹³:

$$R'^{-2n} = (-1)^{n-1} \sum_{k=0}^{\infty} (2k+1) \times [(n-1)! 2^n \cdot R^n \cdot r^n (t^2 - 1)^{(n-1)/2}]^{-1} Q_k^{n-1}(t) \cdot P_k(\cos\theta), \quad (\text{A12})$$

where $Q_k^n(t)$ are the associated Legendre functions of the second kind for argument $|t| > 1$.

The expansion of higher odd powers can be obtained by differentiating Eq. (13). The result is

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