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Fine structure transitions of C⁺ in collisions with H₂

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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 2P½ 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

$$C⁺(2P½) + H₂ → C⁺(2P½) + H₂.$$  (1)

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 Tully⁴ and by Zimmerman and George.⁹

II. INTERACTION POTENTIALS

We regard the hydrogen molecule as a rigid rotator of mass M_H₂ and moment of inertia I with Hamiltonian H_s. If s specifies the orientation of the internuclear axis with respect to axes fixed in space, the eigenfunctions Y_{l_m}^s(γ) of H_s satisfy the equation

$$H_s Y_{l_m}^s(γ) = \frac{l^2}{2I} j_s(j_s + 1) Y_{l_m}^s(γ);$$  (2)

$$Y_{l_m}^s(γ)$$ is a spherical harmonic.

The Hamiltonian of the carbon ion C⁺ can be written

$$H_{c⁺} + V_{LS}(r) = \frac{1}{2} \sum_{i=1}^{5} \frac{1}{r_i} \nabla_{r_i}^2 + \frac{1}{r_i} \nabla_{r_i} \cdot \nabla_{r_i} + \delta E_{z}$$  (3)

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

$$V_{LS}(r) = \sum_{i} f_i(r_i) l_i \cdot s_i,$$  (4)

l_i and s_i being, respectively, the orbital and spin angular momentum of the i-th electron.

The electronic Hamiltonian H_{e}(r) commutes with the electron orbital angular momentum L² and the projection, L_z, of L on a space-fixed axis, and with the spin angular momentum S² and the projection, S_z, of S on a space-fixed axis. Let φ(nLSm_L m_S) be the eigenfunction corresponding to the specified quantum numbers, nLSm_L m_S, labelling the eigenvalue ε(n, L, S). The eigenfunction corresponding to the total angular momentum j_a = L + S can be written as the sum

$$φ(nLSm_L m_S) = \sum_{l_m} C(L, S; j_a; m_S) \phi(nLSm_L m_S),$$  (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

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

Then,

$$\langle j_a m_a | H_{c⁺} + V_{LS} | j_a m_a \rangle = \frac{1}{2} \Delta (j_a(j_a + 1) - L(L + 1) - S(S + 1)) \delta_{l_a l_a} \delta_{m_a m_a},$$  (7)

where we have chosen an energy origin such that ε(01½) = 0.

The Hamiltonian for the interacting C⁺-H₂ system is

$$\mathcal{H} = -\nabla_{r}^2/2μ + H_s(r) + H_{e}(r) + V_{LS}(r, R),$$  (8)

where μ is the reduced mass

$$μ = \frac{M_{H₂}}{M_{H₂} + M_{C⁺}} (M_{H₂} + M_{C⁺}),$$  (9)

and V(r, R) is the electrostatic interaction between C⁺ and H₂. The electronic term H_{e} is the adiabatic Hamiltonian for the CH₂ complex in the Born-Oppenheimer approximation. For a linear approach in which C⁺ approaches H₂ along its internuclear axis, the symmetry is C_{xxx} and there are two adiabatic molecular states, one of ²Σ and one of ²Π symmetry. Both dissociate asymptotically to a product of the states C⁺(²P) and H₂(X'Σ⁺). For perpendicular approach, the symmetry is C_{yy} and there are three adiabatic molecular states, ²Σ, ²Π, and ²Σ⁺.

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 its lowest rotational level j_a = 0 during the collisions. The cross sections are controlled mainly by the interactions at separations of C⁺ and H₂ near 3 Å, where the splitting between the ²Σ and ²Π 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_{xx} symmetry, and we assumed...
that the $C_{av}$ 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 $\phi$ and $\theta$ are the polar coordinates of $R$. Then $\mathcal{C}$ becomes

$$\mathcal{C}(r, R, \theta, \phi) = -\frac{1}{2\pi} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{L^2_{\mu}(\theta, \phi)}{\mu R^2} + H_r + H_{ab} + V_{LS}(r, R),$$

where $L_{\mu}$ is the nuclear angular momentum in body-fixed coordinates,

$$L_{\mu} = iR \times \nabla_R = (J - J_0) = J - L - S,$$

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

$$H_{ab} \Psi_{\Lambda m_\Lambda}(R) = E_{1\Lambda}(R) \Psi_{\Lambda m_\Lambda}(R),$$

where $\Lambda$ is the quantized molecule-fixed projection of $L$ along the intermolecular axis $R$. Thus, the eigenvalues for the molecular complex which dissociates into $C^*(2P)$ and $H_2(1s_{\frac{1}{2}}, j_z = 0)$ are given by

$$E_{1\Lambda}(R) = E_{1\Lambda}^{0}(R) = \left\{ \Psi_{\Lambda m_\Lambda}^{0}(R) \right\} V(r, R) \Psi_{\Lambda m_\Lambda}^{0}(R),$$

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

The potential curves $^2\Sigma$ and $^2\Pi$ of the linear $C^*-H-H$ complex at short and intermediate values of $R$ have been calculated recently by Liskow, Bender, and Schaefer. The long-range part of molecular potentials can be expanded in the form

$$V_{eff}(r, R) = \sum_{n \neq 0} \nu_n(r, R) P_n(\hat{r}, \hat{R}),$$

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

$$\langle \Psi_{1/2, \epsilon_3/2}(R) | H_{ab} + V_{LS} | \Psi_{3/2, \epsilon_3/2}(R) \rangle = E_1 + \frac{3}{2}\Delta, \quad \langle \Psi_{3/2, \epsilon_3/2}(R) | H_{ab} + V_{LS} | \Psi_{1/2, \epsilon_3/2}(R) \rangle = \frac{1}{2}(E_0 + E_3) + \frac{3}{2}\Delta, \quad \langle \Psi_{1/2, \epsilon_3/2}(R) | H_{ab} + V_{LS} | \Psi_{1/2, \epsilon_3/2}(R) \rangle = \frac{1}{2}(E_0 + 2E_3) - \frac{3}{2}\Delta, \quad \langle \Psi_{1/2, \epsilon_3/2}(R) | H_{ab} + V_{LS} | \Psi_{3/2, \epsilon_3/2}(R) \rangle = \pm \sqrt{3}(E_1 - E_0).$$

Thus, the molecular eigenfunctions $\Psi_{1\Lambda}(R)$ yield asymptotically accurate atomic eigenvalues and eigenfunctions.

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

$$E_2(R) = E(\Sigma^+; 000) \frac{1}{R}; \frac{\pi}{2} + \frac{5}{2} \tilde{\nu}_2(R),$$

$$E_1(R) = E(\Pi^+; 000) \frac{1}{R}; \frac{1}{2} - \frac{1}{5} \tilde{\nu}_2(R) \frac{1}{R},$$

Using the results of Appendix A, we obtain for $\tilde{\nu}_0$ and $\tilde{\nu}_2$,

$$\tilde{\nu}_0(R) \sim \frac{\pi}{R}; \frac{\pi}{2} \frac{\alpha_2}{\alpha_1},$$

$$\tilde{\nu}_2(R) \sim \frac{\pi}{R}; \frac{\pi}{2} \frac{\epsilon_2}{\alpha_1} \frac{\alpha_2^2}{\alpha_1},$$

where $\alpha_0$, $\alpha_2$, and $\alpha_2$ are, respectively, the permanent quadrupole moment, and the parallel and perpendicular polarizabilities, and $\langle \nu^2 \rangle$ is the expectation value of $\nu^2$ for $C^*$. It is convenient at this point to introduce molecular complex wavefunctions $\psi_{j\Lambda}(R)$ which become diagonal in both $j^2$ and $j_z$ at infinite separation

$$\psi_{j\Lambda}(R) \sim \Phi_{j\Lambda},$$

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

$$\psi_{j\Lambda}(R) = \sum_{\Lambda m_\Lambda} C(L, j; j, \Lambda, m_\Lambda, \Omega) \Psi_{\Lambda m_\Lambda}(R),$$

in which case

$$E_{1\Lambda}(R) = \sum_{\Lambda m_\Lambda} C(1\mu; 1, \Lambda, \Omega) C(1\mu; 000) \delta_{\Lambda}(R),$$

$\delta_{\Lambda}(R)$ is the expectation value of $\nu_a(r, R)$ for the $2p$ orbital. $C(1s_{\frac{1}{2}}; 000)$ is zero unless $\mu$ is an even integer. If we retain only the first two leading nonvanishing terms in Eq. (16), we have

$$E_2(R) = E(\Sigma^+; |000) + \frac{5}{2} \tilde{\nu}_2(R),$$

$$E_1(R) = E(\Pi^+; |000) - \frac{1}{5} \tilde{\nu}_2(R) \frac{1}{R},$$

Using the results of Appendix A, we obtain for $\tilde{\nu}_0$ and $\tilde{\nu}_2$,

$$\tilde{\nu}_0(R) \sim \frac{\pi}{R}; \frac{\pi}{2} \frac{\alpha_2}{\alpha_1},$$

$$\tilde{\nu}_2(R) \sim \frac{\pi}{R}; \frac{\pi}{2} \frac{\epsilon_2}{\alpha_1} \frac{\alpha_2^2}{\alpha_1},$$

where $\alpha_0$, $\alpha_2$, and $\alpha_2$ are, respectively, the permanent quadrupole moment, and the parallel and perpendicular polarizabilities, and $\langle \nu^2 \rangle$ is the expectation value of $\nu^2$ for $C^*$. It is convenient at this point to introduce molecular complex wavefunctions $\psi_{j\Lambda}(R)$ which become diagonal in both $j^2$ and $j_z$ at infinite separation

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$$\psi_{j\Lambda}(R) = \sum_{\Lambda m_\Lambda} C(L, j; j, \Lambda, m_\Lambda, \Omega) \Psi_{\Lambda m_\Lambda}(R),$$

where $\Psi_{\Lambda m_\Lambda}(R) = \psi_{1\Lambda}^{1/2}(R)$. The spin-orbit operator $V_{LS}(r, R)$ in the representation of $\psi_{j\Lambda}(R)$ can be approximately evaluated by

$$\langle \psi_{j\Lambda}(R) | V_{LS}(r, R) | \psi_{j\Lambda}(R) \rangle \approx \langle \Phi_{j\Lambda} | V_{LS}(r) | \Phi_{j\Lambda} \rangle,$$
C*(2P) + H2(X2Σ+, Jz = 0) = C*(2P) + H2(X2Σ+, Jz = 0) \tag{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 \( E \):

\[
(\mathcal{H} - E) \psi(E) = \left[ -\frac{1}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + \frac{L_R^2}{2\mu R^2} + \left( H_0(r) + V(r, R) + V_LZ(R, R) \right) \right] \psi(E) = 0 . \tag{25}
\]

The asymptotic wavefunctions can be represented by

\[
\psi(E) \sim \sum_\alpha G_\alpha(R) | \alpha \rangle , \tag{26}
\]

where \( | \alpha \rangle \) are the channel states and are eigenfunctions of \( L_R^2/2\mu R^2 \) and of \( (H_0 + V_LZ) \) with eigenvalues \( \epsilon_\alpha \); the radial functions \( G_\alpha(R) \) satisfy

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

We construct molecular channel states \( \psi_\alpha(R) \) with the eigenfunctions \( \psi_\alpha(R) \) of \( (H_0 + V_LZ + V) \) in molecule-fixed coordinates. Because of the \( C_{\mu_\alpha} \) symmetry of the collision system, it is expedient to expand the angular dependence \( \tilde{R} = (\theta, \phi) \) in terms of normalized symmetric-top wavefunctions:

\[
\Omega_{\mu,\Omega}(\theta, \phi) = \sqrt{\frac{2J+1}{4\pi}} D_{\mu_{\Omega}}^{*}\Phi(\phi, \theta, 0) , \tag{28}
\]

where \( M \) is the space-fixed projection of \( J \). The total angular momentum states are then simply constructed as products of \( \Omega_{\mu,\Omega} \) and \( \psi_\alpha(R) \). This procedure yields the molecular channel states \( Z_{J}^{\mu}(r, R) \):

\[
Z_{J}^{\mu}(r, R) = \sum_{\Omega} (-1)^{\mu_\Omega} C(J, J, | \Omega, \Omega, 0 \rangle) \Omega_{\mu,\Omega}(\tilde{R}) \psi_\alpha(R) . \tag{29}
\]

The Clebsch–Gordan coefficients in Eq. (29) show that for a given \( J \) and \( M \), there are at most six channel states if \( C^0 \) is 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 \( Z_{J}^{\mu} \),

\[
\psi_{J}^{\mu}(r) = \sum_{\mu', \Omega} C_{\mu, \mu'}^{\mu, \mu'}(\tilde{R}) Z_{J}^{\mu}(r, R) . \tag{30}
\]

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

\[
\sum_{\mu', \Omega} \langle Z_{J}^{\mu}(r, R) | \mathcal{H} - E | Z_{J}^{\mu'}(r, R) \rangle C_{\mu, \mu'}^{\mu, \mu'}(\tilde{R}) = 0 . \tag{31}
\]

FIG. 1. Molecular potentials for the linear \( C^0 \cdots \text{H} \cdots \text{H} \) 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 \( \langle Z_{J}^{\mu'} | \mathcal{H} | Z_{J}^{\mu} \rangle \) has been discussed by Mies.\textsuperscript{6} If we neglect the angular and radial Born–Oppenheimer matrix elements, the equations reduce to

\[
\left[ \left( -\frac{\hbar^2}{2\mu R^2} - E \right) + U^{J}(r) \right] G(R) = 0 , \tag{32}
\]

where \( G = \{ G_{J, \mu}^{\mu'}(r) \} \) and \( I = \{ \delta_{\mu, \mu'}, 1 \} \). \( Q \) and \( \bar{Q} \) being column vectors, and the interaction matrix \( U^{J}(r) \) is diagonal.

FIG. 2. Oscillatory behavior of the partial cross sections \( Q_{J}^{\mu} \) for fine structure transition \( C^0(2P_{1/2} \to 2P_{3/2}) \) at \( E_{\text{tot}} = 0.0275 \text{ eV} \). The solid line is \( Q_{J}^{\mu} \) and the dashed line is \( Q_{J}^{\mu} \).
This set of coupled differential equations can be solved by standard procedures. The boundary conditions are

\[ \begin{align*}
F_I^t & = 0, \quad (R = 0) \\
F_I^t & = \frac{\delta_{J_J', J_I'} \delta_{II'} \{ -2 i \sin(k_J R - \frac{1}{2} l \eta) \}}{k_J} T^t(I, J; J' I') \exp \left\{ \frac{1}{2} \left[ (k'_J R - \frac{1}{2} \pi) \right] \right\}, \quad (36b)
\end{align*} \]

which defines the \( T \)-matrix which is symmetric in \( (J, I) \) and \((J', I')\).

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

\[
\sigma(j \rightarrow j') \approx \frac{\pi}{(2j + 1)} \sum I \sum J' |T^t(I, J; J' I')|^2
= \sum \left\{ Q_J^t(j \rightarrow j') + Q_J^t(j \rightarrow j') \right\},
\]

(37)

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

**TABLE II.** Spin-change cross sections (in units of \( a_0^2 \)) for \( C^+ (P_f^j) + H \leftarrow C^+ (P_f^j) + H_2 \).

<table>
<thead>
<tr>
<th>( E ) (eV)</th>
<th>( \sigma(\frac{1}{2} \rightarrow \frac{3}{2}) )</th>
<th>( \sigma(\frac{3}{2} \rightarrow \frac{1}{2}) )</th>
</tr>
</thead>
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<tr>
<td>0.01</td>
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</tr>
<tr>
<td>0.20</td>
<td>77.7</td>
<td>40.4</td>
</tr>
</tbody>
</table>

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 \( 4 \Sigma \) and \( 2 \Pi \) potential curves for the linear \( C^+ - H - H \) complex \( \{ R(H-H) = 1.4 a_0 \} \) have been calculated by Lis­kwow, Bender, and Schaefer to out \( R = 4 a_0 \). 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

\[
\langle r^2 \rangle = \langle \psi_C^-(\rho) | r^2 | \psi_C^-(\rho) \rangle = 2.679 a_0^2,
\]

which appears in the long-range potentials, was computed by Weisheit and Lane from Hartree–Fock atomic wavefunctions.
at $E \simeq 0.1$ eV. That the C$^+$ + H$_2$ 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$^+$ + H$_2$ system, and as $R^{-4}$ for the C$^+$ + H system.

The associated cooling rate coefficients for C$^+(Zp^3/Z)$ at a kinetic temperature $T$ K,

$$L(T) = \frac{8kT}{\pi a_0^2} \frac{1}{(4\pi)^{1/2}} \Delta E(j = 3/2 - 1/2) \times \int_0^\infty \sigma(3/2 - 1/2) |E| E \exp(-E/kT) dE,$$

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 $j = 1$.

$$V_{eff} = -\frac{1}{2} \alpha_{ab} E_a E_b = \left[ \alpha_{2s} R^2 + r^2 \left( \frac{3}{2} \alpha_{2s} + \frac{1}{2} \alpha_{2s} \right) \right] - (2Rr \alpha_{2s}) P_1(\cos \theta) + \left[ \frac{3}{2} r^2 (\alpha_{2s} - \alpha_{2s}) \right] P_3(\cos \theta)/R^{16}$$

$$- \frac{2e^2 \alpha_{2s}}{R^4} + \left[ \frac{2e^2 \alpha_{2s}}{R^4}(R - r) P_1(\cos \theta) \right]/R^{13},$$

and

$$V_{eff} = -\frac{1}{2} \Omega_{ab} E_a = e \frac{2 \alpha_2 R^2}{R^{15}} - (2e \alpha_2 Rr/R^{15})$$

$$\times P_1(\cos \theta) + (e \alpha_2 r^2/R^5) P_5(\cos \theta).$$

We wish to expand $V_{eff}$ in terms of Legendre polynomials.

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 H$_2$**

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

$$V_{eff} = -\frac{1}{2} \alpha_{ab} E_a E_b - \frac{1}{2} \Omega_{ab} E_a,$$  \hspace{1cm} (A1)

where $\alpha_{ab}$ and $\Omega_{ab}$ are, respectively, the polarizability and quadrupole moment tensor components of the H$_2$ molecule, and $E_a$ and $E_a$ are, respectively, the electric field and the field gradient at the center of mass of the H$_2$ 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 H$_2$ are

$$\alpha_{ab} = \frac{1}{2} (\alpha_{2s} + 2\alpha_{2s}) \delta_{ab} + \left( \frac{3}{2} \alpha_{2s} - \alpha_{2s} \right) (3 \alpha_{2s} - \delta_{ab}),$$

and

$$\Omega_{ab} = \frac{1}{2} \Omega_{2s} (3 \alpha_{2s} - \delta_{ab}),$$

where $\alpha_{2s}$ and $\alpha_{2s}$ are the parallel and perpendicular components of polarizability of H$_2$, and $\Omega_{2s}$ is the permanent quadrupole moment. The quantities $l_2(\alpha = x, y, z)$ are the direction cosines of the H–H internuclear axis. The long-range interaction (A1) in the linear geometry reduces to

$$V_{eff} = -\frac{1}{2} \left( \alpha_{xx} E_x^2 + \alpha_{yy} E_y^2 + \alpha_{zz} E_z^2 + \frac{3}{2} (\alpha_{2s} - \alpha_{2s}) (3 \alpha_{2s} - \delta_{ab}) \right).$$

Now the electric field $E$ at the center of mass of H$_2$ is

$$E = -\frac{e \hat{R}}{R^{14}} + 2e \hat{R}/R^5,$$  \hspace{1cm} (A3)

where $\hat{R}$ is the unit vector from C$^{+2}$ to the center of mass of H$_2$, and $\hat{R}$ is the unit vector from the 2p electron.

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

$$V_{eff} = V_{eff}^{p} + V_{eff}^{q},$$  \hspace{1cm} (A4)

where

$$V_{eff}^{p} = \sum_{j=0}^{\infty} v_1(R, r) P_1(\cos \theta).$$  \hspace{1cm} (A7)

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

$$R'' = R^2 + r^2 - 2Rr \cos \theta.$$  \hspace{1cm} (A8)
FIG. 4. The geometry and coordinate system for calculating the C⁺⁻ H₂ effective long-range interaction.

and for $r < R$

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