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Molecular Multipole Moments Derived from Collisional Quenching of H(2s)

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Abstract. In this paper we try to improve on existing Born approximation treatments [1] of collisional quenching of metastable hydrogen atoms by molecules in thermal energy collisions. A four-state coupled-channel impact parameter calculation is carried out. The molecule is treated as a static charge distribution whose rotational motion is neglected. Cross-section results from the present calculation are used to calculate new values of multipole moments for CH_3I, N_2, CO_2, and CCl_4 from available experimental data.

I. Introduction

The well-known sensitivity of metastable atomic hydrogen to electric fields makes it a promising tool for the investigation of molecular charge distributions. This possibility was first pointed out by Gersten [1] who calculated cross-sections for

$$\begin{aligned} \mathrm{H}(2s) + \mathrm{M} &\rightarrow \mathrm{H}(2p) + \mathrm{M} \\ &\rightarrow \mathrm{H}(1s) + \mathrm{Ly}-\alpha + \mathrm{M} \end{aligned} \tag{1}$$

in a first-order straight-line trajectory impact parameter approach. To calculate transitions for the above process Gersten replaced the molecule by its lowest-order non-vanishing multipole moment. This simplification is similar to the procedure adopted in calculating van der Waals forces, e.g. with overlap between charge distributions of the interacting systems being neglected. Since the order of magnitude of quenching cross-sections is 10^{-14} cm^2 corresponding to an interaction distance $\geqslant 10^{-7}$ cm, the van der Waals assumption should be well justified.

However, due to the extreme sensitivity of metastable hydrogen to electric fields, a Born approximation treatment of the collision leads to transition probabilities exceeding unity already at these large impact parameters. Gersten, therefore, adopted the standard procedure from line broadening theory and took transition probabilities $P(\rho)$ for impact parameters $\rho \leqslant \rho_0$ equal to one, ρ_0 being the largest root of the equation

$$P(\rho) = 1. \tag{2}$$

We consider this procedure to be formal and unphysical in the present case. From the interaction distance of 10^{-7} cm given above the interaction time for a projectile velocity of 10^6 cm/sec would be of the order of 10^{-13} sec. Comparison of this time with

[1]) Now at Landis & Gyr AG, Zug, Switzerland.

the life time of the $n = 2$ states of atomic hydrogen in a strong electric field $\tau \approx 3.2 \times 10^{-9}$ sec [2] shows that the effect of the collision will only be a thorough mixing of $2s$ and $2p$ states. The decay of the $2p$ state by emission of Lyman–Alpha radiation, which completes the quenching process, takes place when the collision is already over. As a consequence elastic collisions should occur even at impact parameters $\rho \leqslant \rho_0$. This, in turn, would lead to smaller quenching cross-sections.

In Section 2 below we give a short outline of the first-order theory modified by the strong mixing assumption. In Section 3 a coupled-channel solution following the method proposed by Takayanagi [3] and explored by Bauer and Callaway [4] is presented. Results are discussed in Section 4.

We shall use atomic units except where otherwise specified.

II. First-Order Theory

Consider a molecule M approaching a metastable hydrogen atom with velocity $\vec{v}$ (Fig. 1). Let $\vec{R}$ denote the position of the molecule's centre of mass with respect to the hydrogen atom. The angles specifying the direction of $\vec{R}$ are chosen such that $\phi = 0$ is in the direction of $\vec{v}$ and $\theta = \pi/2$ fixes the collision plane. Let χ and ω specify the orientation of the molecule with respect to the collision plane. The interaction matrix element $V_{L'\mu',L\mu}$ for hydrogen states with angular momentum quantum numbers $L'\mu'$ and $L\mu$, respectively ($L' = L \pm 1$) is then given by

$$V_{L'\mu',L\mu} = 4\pi\sqrt{l+1}\, M_l \sum_{\sigma\lambda m} (-1)^{\mu+l-1} \begin{pmatrix} l & 1 & l+1 \\ m & \sigma & \lambda \end{pmatrix} \times \left\langle L'\mu' | r \cdot \sqrt{\frac{4\pi}{3}}\, Y_1^\sigma | L\mu \right\rangle Y_l^m(\chi, \omega) \cdot \frac{Y_{l+1}^\lambda(\theta, \phi)}{R^{l+2}}, \tag{3}$$

r is the radial coordinate in the hydrogen atom and l is the order of the molecule's first non-vanishing multipole moment M_l. In the special case of a $2s\sigma \to 2p\mu$ transition this

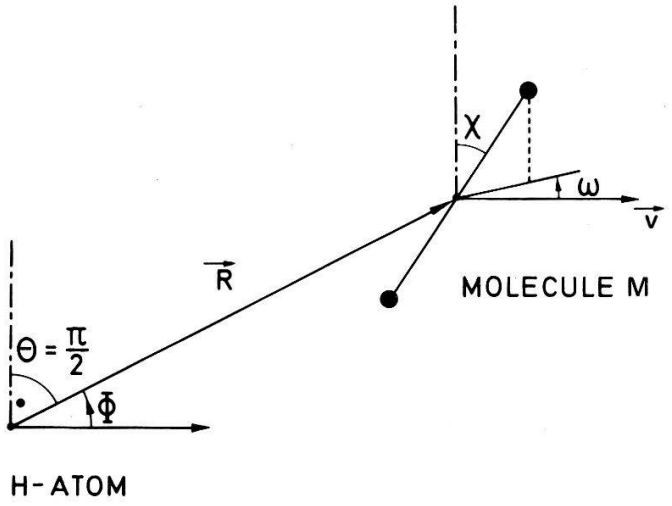

Figure 1
Coordinates used to describe the collision.

expression simplifies to

$$V_{2so,2p\mu} = 12\pi(-1)^{\mu+l-1}\sqrt{l+1}\,M_l \cdot \sum_m Y_l^m(\chi,\omega)\begin{pmatrix} l & 1 & l+1 \\ m & -\mu & \mu-m \end{pmatrix}\frac{Y_{l+1}^{\mu-m}(\theta,\phi)}{R^{l+2}} \tag{4}$$

The first-order transition amplitude is then

$$T_{2so,2p\mu} = \int_{-\infty}^{\infty} V_{2so,2p\mu}\,dt \tag{5}$$

We evaluate $T_{2so,2p\mu}$ in a straight-line trajectory approximation. With

$$\vec{R} = \vec{\rho} + \vec{v}t \tag{6}$$

and coordinates chosen as in Figure 1 the time integration is given by

$$\int_{-\infty}^{\infty} \frac{Y_{l+1}^{\mu-m}\left(\frac{\pi}{2},\phi\right)}{R^{l+2}}\,dt = \begin{cases} 0 \quad \text{for } l+\mu-m = \text{even} \\ (-1)^{(l+1)/2+\mu-m}\,\dfrac{l!}{v\rho^{l+1}}\left\{\dfrac{2l+3}{\pi(l+m+1-\mu)!\,(l+\mu+1-m)!}\right\}^{1/2} \end{cases}. \tag{7}$$

We insert (7) and (4) in (5) and obtain for the first-order transition probability

$$P_{2so,2p\mu} = \left\{\frac{M_l}{v\rho^{l+1}}\right\}^2 (12l!)^2 \cdot \pi(l+1)\,(2l+3) \cdot \left| \sum_m{}' (-1)^{(l+1)/2+\mu-m} \times \begin{pmatrix} l & 1 & l+1 \\ m & -\mu & \mu-m \end{pmatrix} \frac{Y_l^m(\chi,\omega)}{\sqrt{(l+m+1-\mu)!\,(l+\mu+1-m)!}} \right|^2. \tag{8}$$

The sum in this expression is restricted to values of m such that $l+\mu-m =$ odd. The transition probability, of course, diverges for small impact parameters ρ and is replaced by a constant for ρ smaller than some critical impact parameter ρ_K. We define ρ_K by

$$P_{2so,2p\mu}(\rho_K) = \frac{1}{1+K} \tag{9}$$

and obtain the total cross-section as a function of (χ, ω).

$$Q_{2so,2p\mu}^{K}(\chi,\omega) = \frac{1}{1+K}\,\pi\rho_K^2 + 2\pi\int_{\rho_K}^{\infty} P_{2so,2p\mu}(\rho)\,\rho\,d\rho. \tag{10}$$

Finally, we sum over the degeneracy of the $2p$ state and average over molecular orientations

$$Q^K_{2s,2p} = \frac{1}{4\pi} \int \sum_{\mu} Q_{2so,2p\mu}(\chi, \omega)\, d\Omega \tag{11}$$

and obtain

$$Q^K_{2s,2p} = \frac{\pi C_l}{(1+K)^{l/(l+1)}} \left(1 + \frac{1}{l}\right) \left\{\frac{9 \cdot 2^{2l+3}\,(l+1)\,(l!)^2}{(2l+2)!}\right\}^{1/(l+1)} \left\{\frac{M_l}{v}\right\}^{2/(l+1)} . \tag{12}$$

Values of the constants C_l which arises from the numerical integration involved in (11) are given in Table I. Eq. (12) may be modified to obtain Gersten's result taking $K = 0$ and $C_l = 1$.

The choice $K = 0$ corresponds to complete quenching for impact parameters $\rho \leqslant \rho_0$. For reasons given in Section I we propose to assume complete mixing of the $n = 2$ states inside a critical impact parameter, e.g. $K = 1$. This choice reduces the quenching cross-sections by a factor $\sqrt{2}$ for a dipole molecule and by a factor of 2 for $l \to \infty$ as compared to Gersten's result.

A constant $C_l = 1$ is obtained in Gersten's work because he takes the average over molecular orientations and the sum over the degeneracy of the $2p$ state after equation (8). This is certainly incorrect though numerically of minor importance.

III. Unitary Calculation

The method proposed by Takayanagi [3] as described by Callaway and Bauer [4] consists of taking the matrix

$$e^{-iT} \tag{13}$$

with T as defined in (5) as an approximation to the S-matrix. If we take into account only the $n = 2$ states in hydrogen, T has the form

	$2s$	$2p_{-1}$	$2p_0$	$2p_1$
$2s$	0	a	b	c
$2p_{-1}$	a^*	0	0	0
$2p_0$	b^*	0	0	0
$2p_1$	c^*	0	0	0

(14)

The initial state

$$\begin{bmatrix} 2s \\ 2p_{-1} \\ 2p_0 \\ 2p_1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{15}$$

is transformed to the final state

$$\begin{bmatrix} 2s \\ 2p_{-1} \\ 2p_0 \\ 2p_1 \end{bmatrix} = \begin{bmatrix} \cos E \\ ia^+/E \sin E \\ ib^+/E \sin E \\ ic^+/E \sin E \end{bmatrix} \tag{16}$$

with

$$E = \{|a|^2 + |b|^2 + |c|^2\}^{1/2}. \tag{17}$$

From (13) we obtain the transition probability

$$P_{2s\to 2p} = \sin^2 E \tag{18}$$

and

$$E^2 = \sum_{\mu=-1}^{1} |T_{2so2p\mu}|^2. \tag{19}$$

It is worthwhile to recall the Born approximation result (8) which is in the present notation

$$P_{2s\to 2p(\text{Born})} = E^2. \tag{20}$$

With (4) we obtain explicitly

$$E = \frac{12}{v} l! \frac{M_l}{\rho^{l+1}} \sqrt{\frac{\pi}{2l+1}} \left\{ \sum_{\mu=0}^{1} \left| \sum_{m=-l}^{l}{}' \frac{Y_l^m(\chi, \omega)}{\sqrt{(l+\mathrm{m})!\,(l-\mathrm{m})!}} \right|^2 \right\}^{1/2} \tag{21}$$

The prime on the inner summation indicates that m is restricted to values such that $l + \mu - m$ is odd. Using (21) in (18), the total cross-section is obtained by an integration over all impact parameters. The remaining average over molecular orientations must be carried out numerically. The result is

$$Q_l = \tfrac{1}{8}\Gamma\left(\frac{l-1}{l+1}\right) \cos\left(\frac{\pi}{l+1}\right) (24 \cdot l!)^{2/(l+1)} \left(\frac{\pi}{2l+1}\right)^{1/(l+1)} B_l \left\{\frac{M_l}{v}\right\}^{2/(l+1)} \tag{22}$$

with

$$B_l = \int \left\{ \sum_{\mu=0}^{1} \left| \sum_{m=-l}^{l}{}' \frac{Y_l^m(\chi, \omega)}{\sqrt{(l+m)!\,(l-m)!}} \right|^2 \right\}^{1/(l+1)} \sin\chi \, d\chi \, d\omega. \tag{23}$$

Values of B_l are given in Table I.

IV. Results and Discussion

The cross-sections obtained in Sections II and III may be conveniently written as

$$Q_l = \gamma_l \left(\frac{M_l}{V}\right)^{2/(l+1)} \tag{24}$$

Values of γ_l are given in Table I for formula (22), (12) with $K = 0$, and (12) with $K = 1$. Comparison of the last two lines in this table shows that the simple 'strong mixing' estimate of Section II produces results which differ by less than 10% from the much more elaborate coupled-channel calculation. Equation (24), together with Table I, may be

Table I

Numerical constants occurring in formulae (12), (22), and (24) of the text. With M_l in esu and v in cm/sec the cross section is given in cm^2

l	1	2	3	4	Ref.
C_l	0.961	0.913	0.874	0.847	(12)
B_l	4.822	4.304	3.186	2.333	(22)
γ_l	30.8	12.6	8.44	6.72	(12, $K = 0$)
γ_l	21.7	7.9	5.02	3.83	(12, $K = 1$)
γ_l	23.3	8.15	4.90	3.61	(22)

used to calculate multipole moments M_l from experimentally determined quenching cross-sections. Table II lists cross-sections for an impact velocity of 10^6 cm/sec from recent measurements of Dose and Hett [5]. The coupled-channel calculation (Table I, last line) is used to derive multipole moments M_l. Currently recommended values [6] are listed for comparison.

Table II

Absolute quenching cross-sections for an impact velocity $v = 10^6$ cm/sec in units of 10^{-14} cm^2. The respective multipole moments must be multiplied by FACTOR to obtain their values in cgs units

	CH_3I	CO_2	N_2	CCl_4
1	1	2	2	3
Q_l	4.7	2.0	1.2	0.83
M_l	0.84	5.0	2.3	12
M_l, rec	1.6	4.3	1.5	10
FACTOR	10^{-18}	10^{-26}	10^{-26}	10^{-34}

There is a considerable disagreement between present and accepted values for the dipole moment of CH_3I. Though the difficulties associated with pressure measurements of condensable vapours might introduce an appreciable error in the measured cross-section, it is hard to believe that this would account for a factor of two.

The case of CO_2 is much more satisfactory. Noting that published values for the quadrupole moment of this molecule range from 1.7 [7] to 5.9 [8] the agreement, in fact, is good.

A huge amount of data is available for the quadrupole moment of N_2. But again the scatter of values is large, ranging from 0.8 [7] to 3.1 [9]. In the absence of a detailed discussion of the merits of the various methods to determine molecular multipole moments the present value of 2.3 must be considered a reasonable answer.

Only three measurements of the octupole moment of CCl_4 are known at present. Values of 0.55 [10], 1.5 [11], and 3.0 [12] are compatible with our result of 1.2.

The failure of the present method in the determination of the dipole moment of CH_3I precludes any definite conclusions concerning its usefulness. Instead we recall that several more or less serious simplifications have been made.

1) Neglect of molecular rotational motion.
2) Neglect of higher order multipole moments.
3) Complete neglect of dispersion forces.

While we are going to remove the first two restrictions with the aim to improve on the present treatment, a proper treatment of dispersion forces would at present meet with unsurmountable difficulties.

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