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Quenching of metastable He^+ 2*s* ions by molecules

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A time-dependent perturbation theory is used to obtain the cross sections and rates for the quenching of metastable helium ions in collision with molecules (H_2, N_2, O_2, and CO_2). The results are compared with the recent experimental data of Prior and Wang.

I. INTRODUCTION

The study of the deexcitation of the long-lived 2*s* metastable state of atomic hydrogen in collision with noble gases[1-8] and molecules[9-15] has received considerable attention during the recent past, both experimentally and theoretically. At low energies, the main contribution to the quenching of metastable hydrogen comes from the adjacent 2*p* states which are nearly degenerate with the 2*s* state. During the reaction, the transfer from 2*s* to 2*p* state occurs, followed by a radiative transition to the ground 1*s* state to complete the quenching process. The interaction potential responsible for the quenching depends on the nature of collision partners. For molecular targets, the interaction potential, which arises primarily due to the multipolar interactions between permanent moments, is of longer range compared to the spherical targets where the induced moments are responsible for the interaction.

Prior and Wang[16] have recently studied the quenching of $He^+(2s)$ metastable ions in collision with noble target gases and several molecules. The quenching mechanism of $He^+(2s)$ ions is similar to that of $H(2s)$ atoms except for one major difference, i.e., the positive charge of the incident ion. For the quenching of these metastable $He^+(2s)$ ions, one has therefore to consider an additional interaction induced by the Coulomb field of the ion. The total interaction potential is therefore of longer range compared to the neutral projectiles. In some recent work,[17] we have studied the quenching of $He^+(2s)$ metastable ion in collision with spherically symmetric targets (He, Ne, Ar, Kr, and Xe), where we took explicit account of the contribution due to the Coulomb field of the ion (It leads to an additional contribution to the potential varying as r^{-4} and is proportional to the target polarizability.)

In the present work, we extend our earlier work[17] to study the collisional quenching of $He^+(2s)$ metastable ions in collision with molecular targets using a time-dependent perturbation theory. A proper account of the Coulomb effects is also taken in the calculation. The molecules studied are H_2, N_2, O_2, and CO_2 (which all have permanent quadrupole moments). The results for the quenching cross sections and rates are compared with the recent experimental data of Prior and Wang.[16]

II. THEORY

For a collision between a metastable $He^+(2s)$ ion and a molecule, the first-order collision operator is given by[14]

$$S(b) = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\, \exp(iH_0t)V(t)\exp(-iH_0t)\,, \qquad (1)$$

where b is the impact parameter of the collision, H_0 is the unperturbed Hamiltonian, and $V(t)$ represents the total interaction potential between the metastable $He^+(2s)$ ion and the target molecule.

The 2*s* state of the He^+ ion is almost degenerate with the nearby 2*p* states. Like hydrogen,[18] the He^+ ion in this initial mixed state [expressed by linear combinations $(2s \pm 2p)/\sqrt{2}$] will have a permanent dipole moment (of magnitude 1.5 a_0). Being a charged particle, it also possesses a monopole moment (e). These moments on the incident ion can interact with the permanent multipole moments of the target molecule. The multipole-multipole interaction can be expressed as[19]

$$V'(t) = 4\pi \sum_{l_1}\sum_{l_2}\sum_{m_1}\sum_{m_2} \frac{(-1)^{l_2}}{(2l+1)}\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!\,(2l_2+1)!}\right\}^{1/2} \frac{Q_{l_1}Q_{l_2}}{R^{l+1}}\, C(l_1l_2l;m_1m_2m)Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)Y^*_{lm}(\Omega)\,, \qquad (2)$$

where C is the Clebsch-Gordan coefficient, Y's are spherical harmonics, and $l = l_1 + l_2$. Q_{l_1} and Q_{l_2} represent the multipole moments of order l_1 and l_2 of the incident ion and the molecular target, respectively. For the cases studied in the present paper, $l_1 = 0, 1$ and $l_2 = 2$. The magnitude of multipole moment is given by

$$Q_l = \int \rho(r,\theta) r^l P_l(\cos\theta)d\tau\,, \qquad (3)$$

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where ρ is the total charge density of the molecule and P_l are the Legendre polynomials.

Besides the permanent moments in the target molecule, the charge and the dipole of the incident ion can induce moments in the target molecule which will give rise to the polarization potential. The dominant contribution to the polarization potential will, however, come from the charge-induced effects. For a positive ion in a zero angular momentum state interacting with a diatomic molecule, the anisotropic polarization potential[20] is given by[21]

$$V_{\mathrm{pol}}(t) = -\frac{\alpha'}{2R^4} \sum_{m_2} \frac{4\pi}{(2l_2+1)} Y_{l_2 m_2}(\Omega_2) Y_{l_2 m_2}(\Omega) \quad , \tag{4}$$

where α' is the anisotropic polarizability of the target molecule. Combining Eq. (2) and (4), the total interaction potential $V(t)$ may be written as

$$V(t) = V'(t) + V_{\mathrm{pol}}(t) \, . \tag{5}$$

The S matrix, which is related to the matrix elements of the total interaction, is then given by

$$\begin{aligned} \langle 2p, J_2 M_2 | S | J_1 M_1, \tfrac{1}{\sqrt{2}}(2s \pm 2p)\rangle = -\frac{i}{\hbar}\frac{4\pi}{\sqrt{2}} \Bigg\{ \pm \sum_{m_2}\sum_{m} \Big[\tfrac{1}{5} \langle J_2 M_2 | Y_{2m_2}(\Omega_2) | J_1 M_1 \rangle \int_{-\infty}^{+\infty} dt\, e^{i\omega_{J_1J_2}t} \Big(\frac{eQ}{R^3} + \frac{e\alpha'}{2R^4}\Big) Y^*_{2m}(\Omega) \Big] \\ + \sum_{m_2}\sum_{m} \Big[\frac{1}{\sqrt{7}} \langle J_2 M_2 | Y_{2m_2}(\Omega_2) | J_1 M_1 \rangle \int_{-\infty}^{+\infty} dt\, e^{i\omega_{J_1J_2}t} \Big(\frac{DQ}{R^4}\Big) Y^*_{3m}(\Omega) \Big] \Bigg\} \, , \end{aligned} \tag{6}$$

where $\hbar\omega_{J_1J_2}$ is the change in the rotational energy of the molecule, e and D represent the monopole and dipole moment of the incident ion, and Q is the quadrupole moment of the molecular target.

We next square S and average over M_1, and sum over M_2 and J_2, to get the probability as follows:

$$P(b) = \frac{2\pi}{\hbar^2} \Big(\tfrac{1}{25} \sum_{J_2} (2J_2+1) C(J_2 2 J_1; 000)^2 \Big| eQ I^m_2(3) + \frac{e\alpha'}{2} I^m_2(4) \Big|^2 + \frac{D^2Q^2}{7} \sum_{J_2} (2J_2+1) C(J_2 2 J_1; 000)^2 |I^m_3(4)|^2 \Big) \, , \tag{7}$$

where

$$I^\lambda_l(n) = \sum_\lambda \int_{-\infty}^{+\infty} dt\, e^{i\omega_{J_1J_2}t} \frac{Y^*_{l\lambda}(\Omega)}{R^n} \, . \tag{8}$$

Assuming straight-line trajectories and choosing the scattering plane to be $\theta = \pi/2$, one obtains[14,22]

$$I^\lambda_l(n) = \frac{\pi}{2^{(n/2-1)}} \times \frac{|p|^{(n/2-1)}}{vb^{n-1}} \sum_\lambda \frac{Y_{l\lambda}(\pi/2, 0)}{\Gamma[\frac{1}{2}(n+\lambda)]} W_{\lambda/2,\,(1-n)/2}(2|p|) \, , \tag{9}$$

where $p = \omega_{J_1J_2} b/v$, and v is the relative speed. The change in the rotational energy ($\omega_{J_1J_2}$) of the target molecule will be very small. Slocomb *et al.*[15] have therefore neglected it in their calculation on the quenching of the metastable hydrogen with molecules. If we do also, we get for the probability

$$P(b) = \frac{2\pi}{\hbar^2} \Big[\tfrac{1}{25} \Big(e^2Q^2 \sum_m |J^m_2(3)|^2 + \frac{e^2\alpha'^2}{4} \sum_m |J^m_2(4)|^2 + e^2Q\alpha' \sum_m |J^m_2(3) J^m_2(4)| \Big) + \tfrac{1}{7} \Big(D^2Q^2 \sum_m |J^m_3(4)|^2 \Big) \Big] \, , \tag{10}$$

where

$$J^m_K(n) = \int_{-\infty}^{+\infty} dt\, \frac{Y^*_{Km}(\Omega)}{R^n} \, . \tag{11}$$

Carrying out the integration one obtains[23]

$$J^m_K(n) = \frac{1}{\pi v b^{n-1}} \left[\left(\frac{(2K+1)\Gamma(K-m+1)}{\Gamma(K+m+1)} \right)^{1/2} 2^{m-1} \cos\Big(\frac{\pi(K-m)}{2}\Big) \frac{\pi\Gamma(n)\Gamma\big(\frac{K}{2}+\frac{m}{2}+\frac{1}{2}\big)}{\Gamma\big(\frac{K}{2}-\frac{m}{2}+1\big)\Gamma\big(\frac{n-m}{2}\big)\Gamma\big(\frac{n+m}{2}\big)(n-1)2^{n-2}} \right] \, . \tag{12}$$

Combining Eqs. (11) and (12) one obtains

$$P(b) = C_1 b^{-4} + C_4 b^{-5} + C b^{-6} \, , \tag{13}$$

where

$$C_1 = \frac{2}{15}\Big(\frac{eQ}{\hbar v}\Big)^2 , \quad C_4 = \frac{3\pi}{80}\frac{(e^2Q\alpha')}{\hbar^2 v^2} , \quad C = \frac{32}{90}\Big(\frac{DQ}{\hbar v}\Big)^2 + \frac{7\pi^2}{2560}\Big(\frac{e\alpha'}{\hbar v}\Big)^2 \, .$$

The total cross section is given by

$$\sigma(v)=2\pi\int_0^\infty db\, bP(b)\,. \tag{14}$$

As mentioned by Gersten,[14] the cross section diverges for small values of the impact parameter. To evaluate Eq. (14), one therefore uses a cutoff impact parameter. Following Seaton,[24] b_0, the value of b at which the integration should be cut off, is that for which P becomes equal to $\frac{1}{2}$. For all impact parameters b less than b_0, one takes $P(b)=\frac{1}{2}$. Using this procedure, we get

$$\sigma(v)=\pi\left[\frac{b_0^2}{2}+\frac{C_1}{b_0^2}+\frac{2C_4}{3b_0^3}+\frac{C}{2b_0^2}\right]. \tag{15}$$

In the above equation C_1, C_4, and C vary as v^{-2}. b_0 is also a function of velocity. The higher terms omitted in the long-range interaction potential [Eq. (5)] will also lead to a similar v^{-2} dependence, as is evident from Eqs. (11) and (12). Their contribution will, however, be small in comparison to the terms already included in the potential. The deexcitation rate is given by the relation[16]

$$R=\sigma\langle v\rangle\,, \tag{16}$$

where $\langle v\rangle$ is the average velocity.

III. RESULTS AND DISCUSSION

We have calculated the quenching cross sections and rates using Eq. (15) and (16), respectively, for the target molecules, i.e., H_2, N_2, O_2, and CO_2.

Table I gives the results of our calculations for the quenching cross section and rate constant at a velocity of 3.3×10^5 cm/sec for the molecules H_2, N_2, O_2, and CO_2. Here we have compared our results with the experimental results of Prior and Wang.[16] From the table, it is observed that our results are higher compared to the experimental data for H_2, N_2, and CO_2 molecules. For H_2 and N_2 our results are, however, within a factor of 2 of the data, whereas for CO_2 our results are higher by a factor of about 2.7. In all these cases, we notice that the dominant contribution to the cross section comes from the quadrupole interaction. For all the molecules the cross section increases almost linearly with the quadruple moment of the molecule. For the O_2 molecule, our results are much lower than the experimental data. The lower cross section in O_2 compared to the other molecules is primarily due to its low quadrupole moment. Also, the interference between the quadrupole and the polarization interaction leads to a substantial reduction in the total cross section for O_2. This interference effect also tends to reduce the cross sections in N_2 and CO_2 molecules, but for them the quadrupole contribution alone is significantly higher than for the O_2 molecule.

In the above context, it may be mentioned that a Born calculation for the rotational excitation of the O_2 molecule by electron impact by Takayanagi,[25] in which only the long-range interaction was retained, also yielded a very low value of the cross section compared to the corresponding calculation for H_2 and N_2 molecules. Geltman and Takayanagi[26] have pointed out that the effect of short-range interaction may play an important role in O_2 for a certain range of energies. By adopting a simple short-range potential (which is the sum of the electrostatic potentials of the isolated atoms), they have shown that the O_2 cross sections, with the inclusion of a short-range potential, change drastically and become much larger in a certain range of energies. Further, the corresponding change in H_2 and N_2 is insignificant. On the basis of the above study of Geltman and Takayanagi,[26] we also expect that the inclusion of the short-range force in $He^+(2s)+O_2$ quenching

TABLE I. Quenching cross section and rate at velocity 3.3×10^5 cm/sec for He^+ $(2s)$ in collision with H_2, N_2, O_2, and CO_2.

Target	α' (Å^3)	Q^d (10^{-26} esu/cm^2)	σ (10^{-14} cm^2) Present calculation	σ (10^{-14} cm^2) Experiment (Prior and Wang)	R(10^{-9} cm^3 sec^{-1}) Present calculation	R(10^{-9} cm^3 sec^{-1}) Experiment (Prior and Wang)
H_2	0.207[a]	0.651	1.55	1.16	5.14	3.69
N_2	0.497[b]	−1.52	3.25	1.74	10.73	5.52
O_2	0.733[c]	−0.39	0.41	1.91	1.36	6.08
CO_2	1.193[d]	−4.30	9.39	3.60	30.98	11.32

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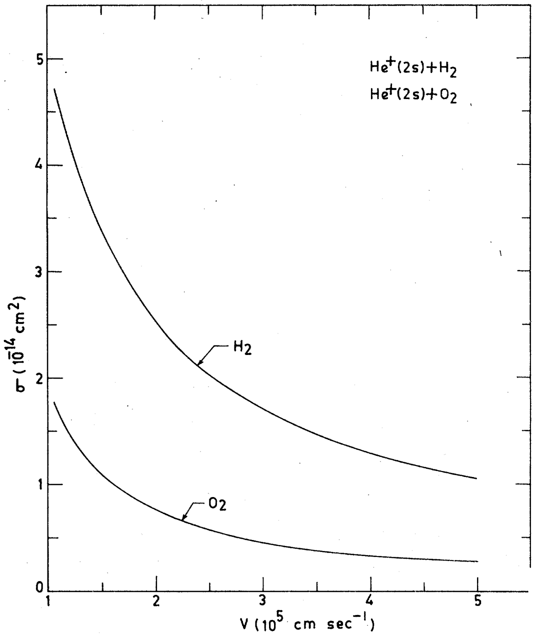

FIG. 1. Velocity dependence of the quenching cross sections for H_2 and O_2 molecules.

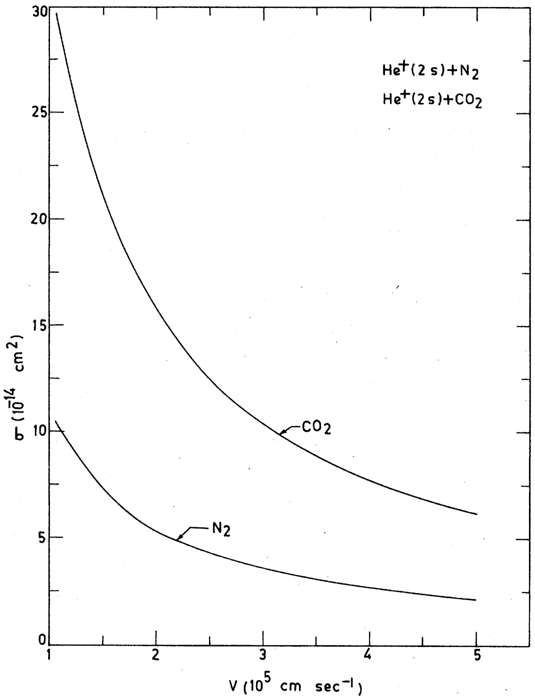

FIG. 2. Velocity dependence of the quenching cross sections for N_2 and CO_2 molecules.

calculation may lead to the enhancement of the cross section. We hope to investigate this in future work.

In our earlier study of quenching with target inert gases,[17] we had found that our results of quenching cross section were within a factor of about 2 compared to the data for all target inert gases. Similar conclusions are obtained here for the study of the quenching with molecular targets (with the exception of O_2 molecule).

The disagreement of the present results with the experimental data, to some extent, may be accounted for if one realizes that there is a 50% inaccuracy in the measurement of velocity as mentioned by Prior and Wang.[16] We have therefore calculated the velocity dependence of the cross section also, which is shown in Figs. 1 and 2. From the figures, it is seen that for small values of the velocity (v), the cross section varies rapidly, and after that a slow variation is noted.

The study on the variation of the cross section with velocity shows that for the case of molecular targets H_2 and N_2 and for the He atom (our earlier paper[17]), the discrepancies between theory and experiment can be largely accounted for by the uncertainties in the experimental measurement of the velocity. For CO_2 and O_2 molecules, however, the variation with velocity is not sufficient to explain the difference between theory and experiment.

It is concluded that the present calculations provide a reasonable estimate of the cross sections and rates when compared with the experimental data of Prior and Wang.[16]

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