Resonant charge exchange between dipole molecules

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Charge exchange between a dipole molecule and its own ion is considered. It is shown that the presence of a dipole moment in the molecule violates the resonant character of the process and considerably changes the charge exchange cross section.

In the analysis of resonant charge exchange between a molecular ion and a diatomic molecule ($AB + AB^+ \rightleftarrows AB^+ + AB$), it is assumed that this process takes place in the same way as the resonant charge exchange of an atom and an ion. In analogy with the calculation of the cross section of charge exchange between an atom and its ion, Bylkin et al.[1] determined the characteristic parameter ρ_0. (The probability of charge exchange W is equal to ½ for impact parameters ρ less than ρ_0, and is negligibly small for $\rho > \rho_0$.) The cross section is $\sigma = \pi\rho_0^2/2$.

Such an analysis is valid for molecules that have no dipole moment. The presence of the dipole moment leads generally to the onset of detuning (exchange interaction) in a given resonant system. Actually, the interaction of the dipole moment of the molecule with the molecular ion, in the principal order in r, is given by $U = e\mathbf{d}\cdot\mathbf{r}/r^3$, where $\mathbf{d}$ is the dipole moment and $\mathbf{r}$ the radius vector of the incident ion (the immobile molecule is located at the origin). In the charge exchange process, the electron succeeds in completing many transitions between the molecule and the molecular ion. Inasmuch as the molecular axes are arbitrarily oriented in space, the interaction of the ion with the dipole of the molecule will depend on which of the charge-exchanging particles has the electron. First one and then the other of the charge-exchanging particles becomes the neutral molecule in the course of the charge exchange.

We denote by $\mathbf{d}_1$ and $\mathbf{d}_2$ the dipole moments of the first and second molecules. The detuning that occurs in this case takes the form

$$\Delta = e(\mathbf{d}_1 - \mathbf{d}_2)\mathbf{r}/r^3. \tag{1}$$

The characteristic order of magnitude is $\Delta \sim \overline{\Delta} = ed/\rho_0^2$.

We now consider collision energies such that one can limit the discussion to rectilinear particle trajectories and the elastic-scattering cross-section is small in comparison with the cross section of resonant charge exchange. We assume the molecular axes to be fixed during the collision. Such a consideration is valid for the following condition on the collision energy ϵ:

$$\varepsilon \gg \varepsilon_{\text{rot}}(\rho_0/a_0)^2, \tag{2}$$

where ϵ_{rot} is the separation of the rotational levels.

Excitation of vibrational levels of the molecule and of the molecular ion was not taken into account. We shall determine at which collision energies such a neglect is valid. The vibrational levels of the molecule and the ion can become excited during collision time for two reasons. First, transitions can arise if the vibrational motion of the nuclei in the molecule and in the ion has no time to react to their translational motion (violation of the adiabatic condition). This imposes a limitation on the collision time, which should be sufficiently large in comparison with the characteristic times of vibration of the nuclei in the molecule and in the ion. This imposes a restriction on the collision energy ϵ:

$$\varepsilon \ll E_0(\rho_0/a_0)^2,\quad E_0 = me^4/\hbar^2. \tag{3}$$

The other reason for the excitation of vibrational levels can be the differences between the vibrational parameters (the characteristic vibrational frequency, equilibrium separation of the nuclei) of the molecule and of the molecular ion. The electron transitions during the course of collision between the particles leads to the appearance of a certain periodic exciting force that acts on the vibrational system. In order of magnitude, the number of electronic transitions during the collision time will be equal to

$$N_1 = \frac{1}{\hbar v}\int_{\rho}^{\infty}\frac{H_{12}(r)\,r\,dr}{(r^2-\rho^2)^{1/2}} \sim \frac{H_{12}(\rho)}{\hbar\gamma v}(\gamma\rho)^{1/2}.$$

Here H_{12} is the overlap integral of the wave functions ($H_{12} \sim E_0e^{-\gamma r}$) and $\gamma^2/2 \equiv E$ is the energy of the electron at the level. The parameter ρ_0 which characterizes the resonant charge exchange is determined (apart from a numerical coefficient) from the condition that the electron succeed in completing at least one transition: For

$$N_1 \sim H_{12}(\rho_0)(\gamma\rho_0)^{1/2}/\hbar\gamma v \sim 1.$$

impact parameters $\rho > \rho_0$, the electron transitions can be neglected. On the other hand, for impact parameters that are comparable with the atomic dimensions ($\rho \sim 1/\gamma$), the number of transitions is equal to $N_2 \sim E_0/\hbar v\gamma$.

Since the contribution to the cross section is made by comparatively large ρ ($1/\gamma \;\underline{\ll}\; \rho \le \rho_0$), the characteristic number of transitions $\overline{N}$ for such impact parameters can be written in the form

$$\overline{N} = (N_1N_2)^{1/2} \sim (v_0/v)^{1/2},$$

where v_0 is the characteristic atomic speed, $v_0 = e^2/\hbar$. The time of the collision is $T \sim \rho_0/v$. Consequently, the characteristic number of electron transitions per unit time is

$$w_n \sim \frac{\overline{N}}{T} \sim \frac{E_0}{\gamma\rho_0}\left(\frac{v}{v_0}\right)^{1/2}.$$

If the characteristic vibrational frequency is much greater than w_n, then transitions between vibrational levels are adiabatically improbable. This is valid for collision energies ϵ

$$\varepsilon \ll E_0(\rho_0/a_0)^4(m/M), \tag{4}$$

where M is the reduced mass of the molecule. The condition (2) and the more stringent of the conditions (3) and (4) determine the range of energies for which our consideration is valid.

We are thus considering charge exchange with a detuning that depends on the relative orientation of the axes of the molecule and of the ion. We calculate the charge exchange cross section for a fixed orientation of the molecular axes (a given detuning), and then average the resultant cross section over all possible orientations of the axes (detunings). We denote by θ_1, φ_1 and θ_2, φ_2 the angles that characterize the position in space of the first and second dipoles. We then rewrite Eq. (1) in the form

$$\Delta = ed[\sin\theta_1(x\cos\varphi_1 + \rho\sin\varphi_1) - \sin\theta_2(x\cos\varphi_2 + \rho\sin\varphi_2)]/r^3, \tag{5}$$

where $x = (r^2 - \rho^2)^{1/2}$ for approaching particles and $x = -(r^2 - \rho^2)^{1/2}$ for particles moving apart.

It is seen from (5) that the detuning Δ is not an even function of s. Inasmuch as the overlap integral of the wavefunctions $H_{12}(\sqrt{x^2 + \rho^2})$ is an even function of x, it then follows that the critical points x_{1cr}, x_{2cr}, which are determined by the equation $|\Delta(x)| = H_{12}(\sqrt{x^2 + \rho^2})$, are generally located at different distances from the turning point (x = 0). This situation is somewhat unusual. For a problem with constant detuning[2] the critical points are naturally symmetrical about the turning point.

The values of the detuning at the critical points, $\Delta_1(x_{1cr})$ and $\Delta_2(x_{2cr})$, are different. We note that this is due not only to the difference between x_{1cr} and x_{2cr}, but more importantly to the fact that the detuning depends on the direction of the radius vector **r** (see (1), (5)). A similar situation, when the values of the detuning at the critical points are different, arises in the solution of the problem of charge exchange in dense gases with account of the effect of the surrounding medium.[3] The formula obtained there for charge exchange with different detunings at the critical points is

$$W = \frac{1}{2}\left(1 - \operatorname{th}\frac{\pi|\Delta_1|}{2\gamma v_{r_1}}\operatorname{th}\frac{\pi|\Delta_2|}{2\gamma v_{r_2}}\right) \quad \text{for } \rho \leqslant \rho_0, \tag{6}$$

where Δ_1 and Δ_2 are the detuning and v_{r1} and v_{r2} are the radial components of the relative velocity at the first and second critical points.

We must next calculate the joint distribution function of the detunings at the two critical points. The calculation is similar to that carried out earlier[3] for charge exchange in dense gases, and the same approximations are used. In contrast with the problem of charge exchange in dense gases, we have succeeded in the present case in calculating the distribution function in explicit form ($z = \rho^2/\rho_0^2$):

$$\begin{gathered} f(\Delta_1, \Delta_2) = [z(1-z)]^{-1/2}\frac{\rho_0^2}{8\pi ed}\left[\operatorname{Arch}\left(4L_1\frac{ed}{\rho_0^2}\right) + \operatorname{Arch}\left(4L_2\frac{ed}{\rho_0^2}\right)\right]; \\ L_1 = [(\Delta_1+\Delta_2)^2/z + (\Delta_1-\Delta_2)^2/(1-z)]^{-1/2}, \\ L_2 = [(\Delta_1+\Delta_2)^2/(1-z) + (\Delta_1-\Delta_2)^2/z]^{-1/2} \end{gathered} \tag{7}$$

for $4ed/\rho_0^2 > 1/L_1$, $1/L_2$.

The charge exchange cross section is of the following form, with logarithmic accuracy:

$$\sigma = 8\pi\int_0^\infty d\Delta_1\int_0^\infty d\Delta_2\int_0^{\rho_0} f(\Delta_1, \Delta_2, \rho)W(\Delta_1, \Delta_2, \rho)\rho\,d\rho. \tag{8}$$

We denote the value of γv by Δ_0. Asymptotically, the charge exchange cross sections for small and large characteristic detunings takes the following form: for $\alpha = \Delta/\bar{\Delta}_0 = ed/\rho_0^2\gamma v \ll 1$, the cross section is

$$\sigma = {}^1/_2\pi\rho_0^2(1 + {}^1/_6\pi^2\alpha^2\ln\alpha^2) + O(\alpha^2), \tag{9}$$

for $\alpha \gg 1$

$$\sigma = 0{,}46\ \rho_0^4\gamma v/ed. \tag{10}$$

The last result can be explained in the following fashion. If $\alpha = \bar{\Delta}/\Delta_0 \gg 1$, the charge exchange cross section is as a rule exponentially small. It becomes comparable with the resonant charge exchange cross section only when the mutual orientation of the dipoles leads to a small detuning (for example, when the vector of the difference of the dipole moments is perpendicular to the collision plane). Multiplying the resonant charge exchange cross section $\rho_0^2/2$ by the collision probability with detuning $\Delta \lesssim \Delta_0 = \gamma v$ (for $\alpha \gg 1$ this probability is of the order of $\Delta_0/\bar{\Delta} \sim \gamma v\rho_0^2/ed$), we obtain Eq. (10) apart from a numerical coefficient.

In conclusion, we estimate the characteristic relative velocity v for which the parameter $\alpha \sim 1$ and the cross section differs significantly from the resonant value. For a CO molecule, we have d = 0.1 at. units and $\alpha \sim 1$ at $v \sim 10^{-2}\,v_0$. These estimates give grounds for believing that it would not be difficult to observe this effect experimentally.

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[2] Yu. I. Demkov, Zh. Eksp. Teor. Fiz. **45**, 195 (1963) [Soviet Phys.-JETP **18**, 138 (1964)].
[3] R. Z. Vitlina and A. M. Dykhne, Zh. Eksp. Teor. Fiz. **64**, 510 (1973) [Soviet Phys.-JETP **37**, 260 (1973)].

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