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DISSOCIATION OF DIATOMIC MOLECULES IN FAST COLLISIONS

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The cross sections for dissociation and for the excitation of higher vibrational and rotational bound states through collisions between atoms and diatomic molecules are calculated for relative-motion energies that considerably exceed the dissociation energy.

1. Diatomic molecules which collide with atoms can undergo dissociation resulting either from electronic transitions or from the direct excitation of higher vibrational and rotational states lying within the continuous spectrum. When the velocities of the incoming particles are of the same order or greater than the velocities of atomic electrons, dissociation results mainly from electronic transitions. At lower velocities the role of electronic transitions is usually reduced sharply; the relative contribution of vibrational level excitation to the dissociation cross section increases and becomes predominant when the collision energy is of the same order as the dissociation energy. The probability of this process has been calculated by Salpeter[1] and Bauer,[2] and by Sayasov and Ivanov [3] for neutron-induced dissociation. Salpeter determined the dissociation cross section of H_2^+ on the basis of the cross section for energy transfer in elastic two-body collisions. Bauer calculated the dissociation cross section of the H_2 molecule for collisions with H atoms in the Born approximation, but without considering the excitation of rotational levels.

In the present work we have used the approximation of sudden perturbations and the Born approximation to calculate the total cross section for the dissociation of diatomic molecules colliding with atoms when the energy of relative motion considerably exceeds the dissociation energy. It is found that the quantum mechanical expression for the cross section almost coincides with the classical cross section in the case of very small ratios of the zero-point energy of molecular vibration to the dissociation energy. However, as the ratio increases a considerable discrepancy appears, which in the case of some molecules amounts to 20%. This difference exists for all energies of the colliding particles and is associated only with the quantum mechanical description of the molecule. We have also calculated the cross section for the excitation of vibrational and rotational states close to the limit of the continuous spectrum. We have considered only collisions in which the electronic states of the colliding particles remain unchanged.

2. The choice of the interaction potential is very important in connection with atom-molecule collisions. We shall consider collisions for which the effective interaction time τ is so small that dissociation can occur only when a very small distance separates the nucleus of the incident atom from one of the molecular atoms. When this distance is small compared with the equilibrium separation r_0 of the molecular nuclei, the interaction of the atom with the molecule can be represented as the sum of interactions with each of the atoms. We shall obtain the distance at which one of the molecular atoms begins to receive sufficient energy for dissociation. If Δp is the momentum transferred to one of the molecular atoms by the incident atom, dissociation requires fulfillment of the condition

$$(\Delta p)^2 / 2M_i \geqslant DM_i / \mu, \tag{1}$$

where μ is the reduced molecular mass, M_i ($i = 1, 2$) are the masses of the molecular atoms, and D is the dissociation energy. Since

$$\Delta p = \left| \int_{-\infty}^{+\infty} \frac{dV}{dR} dt \right| \approx \frac{ZZ_i e^2}{vR_i}$$

(estimated on the basis of a Coulomb interaction) it follows from (1) that the largest impact parameter for which dissociation will occur at a given incident velocity v is given by

$$R_i \approx \left(\frac{\mu}{M_i^2} \frac{Z^2 Z_i^2 e^4}{2Dv^2} \right)^{1/2} \ll r_0, \tag{2}$$

where $Z_i e$ is the charge of the i-th molecular nucleus and Ze is the charge of the incident nucleus. Therefore the investigation of dissociation requires knowledge of the interaction potential for distances not exceeding R_i. At these distances the atom-molecule interaction potential can be represented as the sum of spherically symmetric potentials:

$$V = V_1\left(\left|\mathbf{R} - \frac{\mu}{M_1}\mathbf{r}\right|\right) + V_2\left(\left|\mathbf{R} + \frac{\mu}{M_2}\mathbf{r}\right|\right), \tag{3}$$

where r is the separation of the molecular nuclei and R is the distance between the incident atom and the center of gravity of the molecule. If the molecule consists of heavy atoms, V_1 and V_2 can be represented by either a screened Coulomb potential or Firsov's potential for isolated atoms,[4] because the inner regions of heavy atoms are only slightly distorted by molecular binding. When $R_i \ll \alpha_i^{-1}$, where α_i is the screening constant, V_1 and V_2 are pure Coulomb potentials. It is, of course, necessary that the distance to the turning point R_t be much smaller than R_i. This condition is fulfilled, since $R_t/R_i \sim (D/E_0)^{1/2} \ll 1$, where E_0 is the energy of the incident atom.

3. Since we are considering only the relative velocities of approach that bring about a collision between the incident atom and only one of the molecular atoms, the dissociation cross section can be derived if we know the cross section σ_i for the transfer of a given momentum $\hbar q$ (or a given energy Δ) to each of the molecular atoms and the probability of molecular dissociation $w_i(\Delta)$. The dissociation cross section is then

$$\sigma = \sum_{i=1}^{2} \int_{D}^{E_i} \sigma_i(\Delta) w_i(\Delta) d\Delta, \tag{4}$$

where E_i is the maximum energy transferred to the i-th atom. We shall assume that the elastic scattering cross section $\sigma_i(\Delta)$ is known. Thus, if V_i is the Coulomb interaction potential, in the center of mass of the particle + molecule system we have

$$\sigma_i(\Delta) d\Delta = \frac{2\pi e^4 Z^2 Z_i^2 \mu}{M_i^2} \frac{d\Delta}{\Delta^2}. \tag{5}$$

The dissociation probability $w_i(\Delta)$ can be calculated in a general form, not depending on the kind of interaction potential, in the sudden perturbation approximation. The conditions permitting this approximation are $\tau \ll T$, $\tau \ll t$, where $\tau \sim R_i/v$ is the collision time for dissociation, $T \sim \hbar/D$ is the characteristic time associated with molecular transitions, and $t \sim R_i/v_i$ is the time required for the movement of the dissociated atoms through distances of the order R_i.

Since the cross section for the transfer of large values of Δ decreases rapidly as Δ increases, dissociation occurs mainly through the transfer of the energy $\Delta \sim D$ to a molecule. Consequently, the relative velocity of dissociated atoms is $v_1 \sim (D/\mu)^{1/2}$. The condition $\tau \ll t$ is thus fulfilled for $v \gg (D/\mu)^{1/2}$. The condition $\tau \ll T$ leads to the following limitation of the velocity of relative motion:

$$v \gg (ZZ_i e^2/\hbar)^{1/2} (\mu D/2M_i^2)^{1/4}, \tag{6}$$

whereas (2) gives

$$v \gg (Z^2 Z_i^2 e^4 \mu / 2r_0^2 D M_i^2)^{1/2}. \tag{7}$$

The more severe limitation of the two conditions (6) and (7) must, of course, be used. At the velocities determined by these inequalities we also have simultaneous fulfillment of the conditions for the employment of the potential (3) and the theory of sudden perturbations. It is important that (6) and (7) are milder conditions than the conventional condition for the Born approximation. Thus, for the dissociation of H_2 molecules by particles of charge Ze the use of the Born approximation requires $v \gg Ze^2/\hbar$, whereas (6) and (7) lead to $v \gg 0.1\, Ze^2/\hbar$.

We shall now calculate the dissociation probability $w(\Delta)$ in the sudden perturbation approximation, where the probability of a transition into an interval dE of final states accompanied by the transfer of momentum $\hbar\mathbf{q}$ to the i-th nucleus will be

$$dw_i(q) = \sum_{l} \left| \int \psi_j^*(\mathbf{r}) \exp\left(i\frac{\mu}{M_i}\mathbf{q}\mathbf{r}\right) \psi_i(\mathbf{r})\, d\mathbf{r} \right|^2 dE, \tag{8}$$

where

$$\psi_i(\mathbf{r}) = \left(\frac{2\beta}{\pi r_0^2}\right)^{1/4} \frac{1}{2\sqrt{\pi} r} \exp\left[-\frac{\beta}{r_0^2}(r - r_0)^2\right] \tag{9}$$

is the wave function of the molecule in its vibrational and rotational ground states;

$$\psi_f(\mathbf{r}) = \left(\frac{2\mu}{\pi\hbar}\right)^{1/2} \frac{1}{r\sqrt{p(r)}} \sin\left[\frac{1}{\hbar}\int_{r_1}^{r} p(r)\, dr + \frac{\pi}{4}\right]$$

$$\times \frac{\sin[(l + 1/2)\theta + \pi/4]}{\sqrt{\sin\theta}} \tag{10}$$

is the quasiclassical wave function corresponding to the final state of the dissociated molecule. Here $\beta = \mu\omega r_0^2/2\hbar \gg 1$, where ω is the vibrational frequency of the molecules;

$$p(r) = \left\{2\mu\left[E - U(r) - \frac{\hbar^2(l + 1/2)^2}{2\mu r^2}\right]\right\}^{1/2};$$

U(r) is the electronic ground term; E is the relative energy of molecular atoms in the final state.

We shall use the results obtained in[5], where the integral in (8) was calculated. After integrating over E and replacing the summation over l by an integral, we obtain

$$w_i(q)=\frac{1}{4\gamma_i(2\pi\beta)^{1/2}}\int\limits_{U_0/\varepsilon_0-\gamma_i^2}^{\infty} dz\int\limits_{1/\gamma_i^2}^{\infty}\frac{dt}{t}\exp\left(-\frac{z^2t}{8\beta}\right), \tag{11}$$

where

$$\gamma_i=\mu r_0 q\,/\,M_i,$$

$$\varepsilon_0=\hbar^2\,/\,2\mu r_0^2,$$

$$U_0=D+{}^1/_2\hbar\omega.$$

Considering that in the c.m. system of the molecule the energy transferred to the i-th atom is

$$\Delta=\frac{\mu}{M_i}\,\frac{\hbar^2q^2}{2M_i}=\gamma_i^2\,\varepsilon_0,$$

after integrating over z we obtain for the dissociation probability

$$w(\Delta)=\frac{1}{4}\Delta^{-1/2}\int\limits_0^{\Delta}\frac{dx}{(\Delta-x)^{1/2}}\left\{1-\Phi\left[\frac{U_0-\Delta}{[2\hbar\omega(\Delta-x)]^{1/2}}\right]\right\},$$

$$\Phi(x)=\frac{2}{\sqrt{\pi}}\int\limits_0^{x}e^{-t^2}\,dt. \tag{12}$$

4. The total dissociation cross section, which is obtained by substituting (12) and (5) into (4), can also be obtained in the Born approximation. Since this approximation corresponds to large collisional velocities ($v \gg ZZ_ie^2/\hbar$), it follows from (2) that dissociation will occur only if the incident atom approaches very close to the molecular atoms. This indicates that the interaction potential can be adequately represented by a Coulomb potential or, more generally, by a screened Coulomb potential. In the c.m. particle + molecule system the differential dissociation cross section is

$$d\sigma=\frac{2\pi}{\hbar}|V_{if}|^2\,\delta\left(\frac{p^2-p'^2}{2M}-D-E\right)dE\,d\mathbf{p}', \tag{13}$$

$$V_{if}=(2\pi\hbar)^{-3/2}\left(\frac{M}{p}\right)^{1/2}\iint\psi_f^*(\mathbf{r})\,V(\mathbf{r},\mathbf{R})$$

$$\times\exp\left[\frac{i}{\hbar}(\mathbf{p}-\mathbf{p}')\mathbf{R}\right]\psi_i(\mathbf{r})\,d\mathbf{r}\,d\mathbf{R}. \tag{14}$$

Here p and p′ are the momentum of the incident particle before and after scattering; M is the reduced mass of the particle + molecule system; ψ_i and ψ_f are the wave functions given by (9) and (10); $V(\mathbf{r}, \mathbf{R})$ is the interaction potential in the form (3) with $V_i(\rho) = ZZ_ie^2\rho^{-1}e^{-\alpha_i\rho}$, where α is the screening constant. Substituting the wave functions into (14) and integrating over $\mathbf{R}$, we obtain

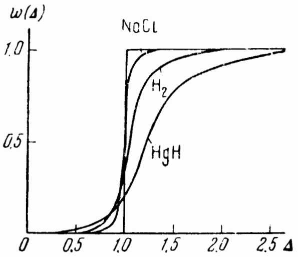

FIG. 1.

$$V_{if}=\left(\frac{2\beta}{\hbar}\right)^{1/4}\left(\frac{\mu}{\pi\hbar v}\right)^{1/2}\frac{2Ze^2\mu^2r_0^3}{\pi\hbar^2}$$

$$\times\left[\frac{Z_1I_1}{M_1^2(a_1^2+\gamma_1^2)}+\frac{Z_2I_2}{M_2^2(a_2^2+\gamma_2^2)}\right],$$

$$I_{1,2}=\int\limits_0^{\pi}\sqrt{\sin\theta}\,\sin\left[\left(l+\frac{1}{2}\right)\theta+\frac{\pi}{4}\right]\int\limits_{x_1}^{\infty}\sin\left[\int\limits_{x_1}^{x}p(x)\,dx+\frac{\pi}{4}\right]$$

$$\times\exp[-\beta(x-1)^2\mp i\gamma_{1,2}x\cos\theta]\frac{d\theta\,dx}{\sqrt{p(x)}}.$$

$I_{1,2}$ has been calculated in [5]. Substituting V_{if} into (13) and integrating over the final states, we obtain

$$\sigma=\frac{\pi Z^2e^4\mu}{4v^2}\sum_{i=1}^{2}\frac{Z_i^2}{M_i^2}\int\limits_D^{\infty}\frac{\Delta^{-1/2}\,d\Delta}{(b_i^2+\Delta)^2}\int\limits_0^{\Delta}\frac{dx}{(\Delta-x)^{1/2}}$$

$$\times\left\{1-\Phi\left[\frac{U_0-\Delta}{[2\hbar\omega(\Delta-x)]^{1/2}}\right]\right\}. \tag{15}$$

In this expression we can neglect the quantity $b_i = \mu\hbar^2\alpha_i^2/M_i^2$, which represents a negligibly small screening effect.

The Born approximation and the theory of sudden perturbations therefore yield the same result for velocities that permit the assumption of a Coulomb interaction potential, although these velocities can be much lower than the limit imposed by the Born approximation. We arrive at this result because the formula representing the cross section for the transfer of the energy Δ in the case of a Coulomb interaction is of the same form at both high and low velocities. The two approximations differ at low velocities:

$$\frac{ZZ_ie^2}{\hbar}>v\gg\left(\frac{ZZ_ie^2}{\hbar}\right)^{1/2}\left(\frac{\mu D}{2M_i^2}\right)^{1/4}$$

in the case of a non-Coulomb interaction potential.

5. For an arbitrary interaction (3) the total dissociation cross section is given by (4), where $w(\Delta)$ is independent of the kind of interaction potential. Equation (4) can be used to calculate the cross section for neutron-induced dissociation

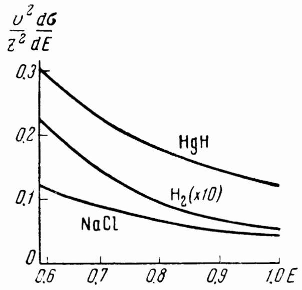

FIG. 2.

after making the substitution $d\sigma(\Delta) = \sigma_0 E_0^{-1} d\Delta$, where σ_0 is independent of Δ. The form of $w(\Delta)$ is shown in Fig. 1 for NaCl, H_2, and HgH; Δ is given in units of D for each case. The ratio $\hbar\omega/2D$ for these molecules is 0.006, 0.061, and 0.231, respectively. For $\hbar \rightarrow 0$, Eq. (12) for $w(\Delta)$ goes over into the classical result: $w(\Delta) = 0$, $\Delta < D$ and $w(\Delta) = 1$ for $\Delta \geq D$.

The classical dissociation probability is represented in Fig. 1 by a step function. Equation (12) shows that the step lacks precise definition within $\sim(\hbar\omega/2D)^{1/2}$. When $\sigma(\Delta)$ is determined from the Coulomb interaction (5), the classical dissociation cross section will be

$$\sigma_{\mathrm{cl}} = \frac{2\pi Z^2 e^4 \mu}{v^2 D}\left(\frac{Z_1^2}{M_1^2} + \frac{Z_2^2}{M_2^2}\right). \tag{16}$$

We note that the dissociation cross section $\sigma = \pi(R_1^2 + R_2^2)$ based on (2) agrees with (16) except for a numerical coefficient.

In the present case the quantum mechanical dissociation cross section will differ from the classical result only by a coefficient depending on the molecular parameters ω and D:

$$\sigma_{\mathrm{qu}} = \alpha(\omega, D)\sigma_{\mathrm{cl}}, \qquad \alpha(\omega, D) = \int_1^\infty \Delta^{-2} w(\Delta)\, d\Delta. \tag{17}$$

Here Δ is given in units of D. For example, in the cases of NaCl, H_2, and HgH we have $\alpha = 1$, 0.9, and 0.8, respectively. Therefore the difference between the quantum mechanical and classical cross sections is sometimes as large as 20%, although the difference is only a few percent for most molecules. For neutron-induced dissociation the difference is unimportant (when $E_0 \gg D$), because the cross section for the transfer of energy Δ is independent of Δ, and the total dissociation cross section is given by

$$\sigma = \frac{\sigma_0}{E_0}\int_D^{E_0} w(\Delta)\, d\Delta \approx \sigma_0 \frac{E_0 - D}{E_0}.$$

This result agrees with [3].

6. The foregoing formulas can be used to determine the cross sections for the excitation of higher vibrational and rotational states. This is possible because the energy spectrum of these states is close to the continuous spectrum, and their wave functions can also be represented by (10). Utilizing (4), (5), and (8) and performing integrations analogous to the foregoing, we obtain the following differential cross section for the excitation of bound states:

$$\frac{d\sigma}{dE} = \sqrt{\frac{\pi}{2}}\,\frac{\mu Z^2 e^4}{v^2\sqrt{\hbar\omega D}}\left(\frac{Z_1^2}{M_1^2} + \frac{Z_2^2}{M_2^2}\right) \times \int_0^\infty \frac{d\Delta}{\Delta^{5/2}}\left\{-\operatorname{Ei}\left[-\frac{2D}{\hbar\omega}\frac{(E-\Delta)^2}{4\Delta}\right]\right\}, \tag{18}$$

where

$$-\operatorname{Ei}(-x) = \int_x^\infty \frac{e^{-t}}{t}\, dt;$$

E is the excitation energy measured from the bottom of the potential well $V(r)$; E and Δ are given in units of D. Figure 2 represents the calculated values of $v^2 Z^{-2} d\sigma/dE$ for NaCl, H_2, and HgH molecules, with v given in units of $e^2/\hbar$ and σ in units of πa_0^2.

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