

## THE INTERACTION OF OPTICALLY ACTIVE MOLECULES

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The discrimination energy between two optically active molecules is calculated using a non-perturbative method. Results of Craig and coworkers emerge as a limiting case.

Craig et al. [1, 2] have recently calculated the dispersion energy between two optically active molecules using quantum mechanical perturbation theory. In this note we derive this energy by a simpler semi-classical non-perturbative method. Our treatment is a generalization of earlier work by Mitchell et al. [3, 4].

The interaction energy arises from mutually induced polarization. Following [1, 2] we define a space coordinate system with origin at dipole 1 and positive  $Z$  axis along the line joining the two dipoles. The principal axes of the polarization tensor of each dipole have arbitrary orientation with respect to the space coordinates. If  $P(1, t) = P(1)e^{-i\omega t}$  and  $M(1, t) = M(1)e^{-i\omega t}$  are the instantaneous electric and magnetic dipole moments of molecule 1, the electric and magnetic fields at the second dipole are

$$E(1, t) = \mathbf{T}P(1)e^{-i\omega t}; \quad H(1, t) = \mathbf{T}M(1)e^{-i\omega t} \quad (1)$$

where for non retarded interactions

$$\mathbf{T} = -r^{-3}(\mathbf{1} - 3\hat{r}\hat{r}). \quad (2)$$

We now specify the response of our molecules to these fields according to constitutive equations suggested by Condon [5]. Thus:

$$P(2) = \alpha(2)E(1) + i\omega\beta(2)H(1), \quad (3)$$

$$M(2) = -i\omega\beta(2)E(1) + \mu(2)H(1). \quad (4)$$

$\alpha$ ,  $\beta$  and  $\mu$  are the electric polarizability tensor, optical-

rotatory pseudo tensor and magnetic polarizability tensor in the space coordinates. We can now eliminate the fields  $E$  and  $H$  from eqs. (1), (3) and (4) to obtain

$$\Gamma(2) = \Omega(2)\Gamma(1), \quad (5)$$

where

$$\Gamma(\alpha) = \begin{bmatrix} P(\alpha) \\ M(\alpha) \end{bmatrix}; \quad \Omega(2) = \begin{bmatrix} \alpha(2)\mathbf{T} & i\omega\beta(2)\mathbf{T} \\ -i\omega\beta(2)\mathbf{T} & \mu(2)\mathbf{T} \end{bmatrix}. \quad (6)$$

Molecule 2 in turn polarizes molecule 1. We immediately obtain the following dispersion relation for allowed modes

$$D(\omega) = \text{Det} [\mathbf{1} - \Omega(1)\Omega(2)] = 0. \quad (7)$$

In terms of this dispersion relation, the complete interaction is [6]

$$V(r) = (\hbar/2\pi) \int_0^{\infty} d\xi \log D(i\xi). \quad (8)$$

The dispersion relation and interaction energy simplify if we assume  $r$  is large ( $\alpha/r^3$ ,  $\omega\beta/r^3$ ,  $\mu/r^3 \ll 1$ ). Substituting (7) into (8) we then expand the logarithm and retain the leading term. Thus

$$V(r) \approx (\hbar/2\pi) \int_0^{\infty} d\xi \text{Tr} \{ -\alpha(1)\mathbf{T}\alpha(2)\mathbf{T} + 2\xi^2\beta(1)\mathbf{T}\beta(2)\mathbf{T} - \mu(1)\mathbf{T}\mu(2)\mathbf{T} \}. \quad (9)$$

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The first term yields the usual London dispersion energy. The third term is the magnetic dispersion energy which we shall not consider further here. The second term yields the discrimination energy since  $\beta$  is different for dextro and laevo optical isomers of the same molecular species.

Following Craig we now assume that each molecule is free to rotate about one of its body axes, say  $Z'$ . After averaging over the appropriate angles, the discrimination energy is

$$\bar{V}_{\text{disc}}(r) = (\hbar/2\pi)(2/r^6)(\cos\gamma - 3\cos\theta_1\cos\theta_2)^2 \times \int_0^\infty d\xi \beta_{33}(1)\beta_{33}(2). \quad (10)$$

$\gamma$  is the angle between the two molecular body  $Z'$  axes.  $\theta_1$  and  $\theta_2$  are the angles between the body  $Z'$  axes and the common space  $Z$  axis. Now we take  $\beta_{33}$  to be of the form

$$\beta_{33}(\alpha) = \sum_n \frac{2R_n(\alpha)\hbar\omega_n^2(\alpha)}{1 + [\xi/\omega_n(\alpha)]^2}, \quad (11)$$

where  $R_n$  is the rotational strength for the absorption of frequency  $\omega_n$ . Substituting (11) into (10) and doing the  $\xi$  integral yields finally

$$\bar{V}_{\text{disc}}(r) = (2/r^6)(\cos\gamma - 3\cos\theta_1\cos\theta_2)^2$$

$$\times \sum_{m,n} \frac{R_m(1)R_n(2)}{\hbar[\omega_m(1) + \omega_n(2)]}. \quad (12)$$

This is identical with the results of Craig and co-workers (see eq. (2.21), ref. [2]). We note that like isomers repel, unlike isomers attract each other.

The method used here can be readily extended to more complex systems. Retardation effects can also be treated. These additional features will be discussed elsewhere.

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