

## THE OPTICAL ACTIVITY OF METHANE

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We examine whether a methane molecule is optically active by virtue of its rotation. We conclude that methane gas at room temperature can be regarded as an enantiomeric mixture of two components, each of which rotates the plane of light by about  $1 \text{ rad m}^{-1}$  but in opposite directions.

The methane molecule has an electric dipole moment in its ground electronic and vibrational state [1]. It arises from the effects of molecular rotation reducing the tetrahedral molecule to axial symmetry; the effect is small and the magnitude of the dipole is only about  $10^{-6} \text{ D}$ . The question raised by this interesting observation is whether methane also shows other properties which simple ideas appear to exclude. The property to which we address ourselves in this note is whether methane is optically active as a result of its rotation.

The classical argument underlying the optical activity can be stated quite concisely. A molecule is optically active if its polarizability differs for right and left circularly polarizable light. A molecule rotating in the same sense as the electric vector of the light might have a polarizability different from that of counter-rotating molecule. Therefore a gas of methane molecules rotating in one sense will rotate plane polarized light. Of course an equilibrium ensemble of methane molecules rotates in both senses, and so the net activity is zero. Nevertheless it remains true that ordinary methane is properly regarded as optically inactive not because of the intrinsic inactivity of the molecules but because it is an enantiomeric mixture. Alternatively one can envisage an application of the birefringent properties of the molecules to a sorting process involving laser light scattering from a molecular beam.

The magnitude of the intrinsic activity can be calculated without much difficulty. We consider a molecule in the state  $|0, JKM\rangle$  with the space-fixed  $z$ -axis along the direction of propagation of the light. For a path length  $\mathcal{L}$  through a sample of number density  $\mathcal{N}$ , assuming a Lorentz local field correction, the angle of rotation is [2]

$$\delta\phi = (\mathcal{L}\omega/2c) (n_{T+} - n_{T-}) = (i\mathcal{L}\mathcal{N}\omega/4c\epsilon_0) (\alpha_{yx} - \alpha_{xy}),$$

where  $\omega$  is the frequency of the light and  $\alpha$  is the polarizability tensor. Note that this result relies on only electric dipole interactions, unlike conventional optical activity which requires one magnetic dipole interaction. In normal circumstance (non-rotating molecules)  $\alpha$  is symmetric and so  $\delta\phi = 0$ ; in the presence of rotation it is not symmetric.

The polarizability tensor in the presence of light of frequency  $\omega$  is [2]

$$\alpha(\omega) = (1/\hbar) \sum_n [d_{0n}d_{n0}/(\omega_{n0} + \omega) + d_{n0}d_{0n}/(\omega_{n0} - \omega)]$$

and introduction of the spherical tensor components  $-er_{\pm 1}^{(1)} = \mp 2^{-1/2} (d_x \pm id_y)$  (and  $-er_0^{(1)} = d_z$ ) leads to

$$\delta\phi = (e^2\omega^2\mathcal{L}\mathcal{R}/2\hbar c\epsilon_0) \sum_n (\omega_{n0}^2 - \omega^2)^{-1} (r_{+1,0n}^{(1)}r_{-1,n0}^{(1)} - r_{-1,0n}^{(1)}r_{+1,n0}^{(1)})$$

The matrix elements can be evaluated by standard angular momentum techniques, and  $n$  should be interpreted as the states  $|n, J'K'M'\rangle$  accessible from the state  $|0, JKM\rangle$ . In tetrahedral symmetry (which is assumed to be maintained throughout) the transition dipoles between electronic states are isotropic in the sense that  $\langle 0|r_q^{(1)}|n\rangle\langle n|r_{-q}^{(1)}|0\rangle = (-1)^q|z_{0n}|^2 r_q^{(1)}$  now being components in the rotating molecular frame. Then since

$$\langle n', J'K'M'|T_Q^{(k)}|n, JKM\rangle = i^{J'+J-K'-K}(-1)^{J'-M'}[(2J'+1)(2J+1)]^{1/2}$$

$$\times \begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix} \begin{pmatrix} J' & k & J \\ -M' & Q & M \end{pmatrix} \langle n'|T_{K'-K}^{(k)}|n\rangle$$

after some manipulation we arrive at

$$\delta\phi = \frac{e^2\omega^2\mathcal{L}\mathcal{R}}{2\hbar c\epsilon_0} \frac{M}{2J+1} \sum_n |z_{0n}|^2 \left[ -\frac{2J-1}{J} \frac{1}{\omega_{J-1n,J0}^2 - \omega^2} - \frac{2J+1}{J(J+1)} \frac{1}{\omega_{Jn,J0}^2 - \omega^2} + \frac{2J+3}{J+1} \frac{1}{\omega_{J+1n,J0}^2 - \omega^2} \right]$$

In this expression  $\omega_{J-1n,J0} = \omega_{n0} - 2BJ$ ,  $\omega_{Jn,J0} = \omega_{n0}$ , and  $\omega_{J+1n,J0} = \omega_{n0} + 2B(J+1)$ , where  $B$  is the rotational constant and  $\hbar\omega_{n0}$  are the electronic excitation frequencies.

We now obtain an approximate form of the last equation by retaining only terms first-order in the rotational energy [we take  $(2BJ)^2 \ll (\omega_{n0}^2 - \omega^2)$ ]. Then one obtains the simple result

$$\delta\phi \approx -M \left( \frac{4Be^2\omega\mathcal{L}\mathcal{R}}{\hbar c\epsilon_0} \right) \sum_n \frac{\omega\omega_{n0}|z_{0n}|^2}{(\omega_{n0}^2 - \omega^2)^2}$$

As expected, different signs of rotation are predicted for different senses of rotation of the molecules (different signs of  $M$ ). Henceforth we shall write the coefficient of  $M$  as  $\mathcal{R}$  so that

$$\delta\phi = M\mathcal{R}$$

The magnitude of  $\delta\phi$  can be estimated as follows. For a 1 m path length through a gas at 1 atm pressure at room temperature, taking  $B = 5.24 \text{ cm}^{-1}$ , using 600 nm light, supposing that  $\omega_{n0} \approx 2\omega$ , and with  $|ez_{0n}| \approx 3 \times 10^{-30} \text{ C m}$ , gives  $\delta\phi \approx 2 \text{ rad}$  when  $M = 10$ .

This calculation can be extended to a symmetric top and the angle of rotation then depends on the quantum number  $K$  as well as  $M$ , but no significant differences appear.

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## References

- [1] L. Ozier, Phys. Rev. Letters 27 (1971) 1329.
- [2] P.W. Atkins, Molecular quantum mechanics (Clarendon Press, Oxford, 1970).