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Some equations for multipole-induced dipole absorption in linear molecules

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The general theory [1] of bimolecular collision-induced infra-red absorption in linear molecules is applied to the particular cases of dipole, quadrupole, octupole, and hexadecapole-induced dipole absorption. Some of the resulting equations are used to reproduce the profile and intensity of the far infra-red (20–400 cm^{-1}) absorption measured by Bosomworth and Gush [4] in compressed gaseous oxygen. From this fit, values of $|Q| = 1{\cdot}0 \times 10^{-40}$ C m^2, and $|\Phi| = 3{\cdot}7 \times 10^{-60}$ C m^4 are derived for oxygen.

1. INTRODUCTION

This work aims to extend the general theory [1] of multipolar-induced dipole absorption in linear molecules to the specific case of the dipole, quadrupole, octupole and hexadecapole components of the field at one molecule due to its neighbour. The resultant equations include a term proportional to the anisotropy of polarizability, which arises from the double transitions corresponding to $\Delta J_1 \geqslant \Delta J_2 = 2$.

The theory is applied to the case of compressed oxygen gas, whose absorption, observed by Bosomworth and Gush [4] in the region 20–400 cm^{-1}, could not be satisfactorily explained on the basis of quadrupole-induced dipole absorption alone. It is found that the overall experimental profile is reproduced fairly well by the use of profiles calculated on the basis of quadrupole and hexadecapole-induced dipolar absorption. Values of $|Q|$ and $|\Phi|$, the quadrupole and hexadecapole moments, respectively, are obtained from the best fit to the experimental intensity and band shape.

A justification for the use of the very short range (R^{-12} dependent) hexadecapole field is based on the evaluation [2] of the approximate range of the induced dipole moment.

2. THEORY

Frost [1] has recently given the formal theory of multipole-induced dipole absorption in linear or symmetric top molecules on bimolecular collision. The basic equation for the intensity (I_{AA}) of the bimolecular collision-induced

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absorption in a single transition J has been given by van Kranendonk [2] and later by Colpa and Ketelaar [3] as

$$I_{\mathrm{AA}} = \frac{4\pi^3 \bar{\nu} N^2}{3hc} \cdot \sum_{\substack{i,f \\ [E_f - E_i \doteqdot h\nu]}} \left(\frac{F_i^{\mathrm{AA}}}{d_i^{\mathrm{AA}}} - \frac{F_f^{\mathrm{AA}}}{d_f^{\mathrm{AA}}} \right) \int_0^\infty 4\pi R^2 \exp\left(-U_{\mathrm{AA}}(R)/kT\right)$$

$$\times \sum_{m_i,\, m_f} |\langle im_i | \boldsymbol{\mu}^{\mathrm{AA}}(R) | fm_f \rangle|^2 \, dR, \qquad (1)$$

where $\boldsymbol{\mu}(R)$ is the induced dipole moment of a pair of molecules separated by a distance R, and where $|im_i\rangle$, $|fm_f\rangle$ denote in general vibration–rotation eigenstates for the pair, with m_i, m_f as degenerate magnetic quantum numbers. The quantities d_i and d_f are the degeneracies of the quantum numbers i, f respectively, $U_{\mathrm{AA}}(R)$ is a convenient form of the intermolecular potential energy.

For linear molecules, it can be shown that [5]

$$\sum_{\substack{i,f \\ [E_f - E_i \approx h\nu]}} \left(\frac{F_i^{\mathrm{AA}}}{d_i^{\mathrm{AA}}} - \frac{F_f^{\mathrm{AA}}}{d_f^{\mathrm{AA}}} \right) = \frac{1}{Z} \exp\left(-E_i/kT\right)\left(1 - \exp\left(-hc\bar{\nu}_{if}/kT\right)\right)$$

where, for linear molecules $Z = \sum_J (2J+1) \exp\left(-hcBJ(J+1)/kT\right)$ (usual notation) is the rotational partition function.

The matrix elements $\sum |\langle im_i | \boldsymbol{\mu}^{\mathrm{AA}}(R) | fm_f \rangle|^2$ are expanded by Frost (his equation (24)) as

$$\sum_{\lambda_1 \lambda_2} \Big[\big(\sum |F_m|^2\big) \frac{(2J_1+1)}{2\lambda_1+1} \cdot C(J_1, \lambda_1, J_1' \,;\, K_1, K_1' - K_1, K_1')^2$$

$$\cdot \frac{(2J_2+1)}{2\lambda_2+1} \cdot C(J_2, \lambda_2, J_2' \,;\, K_2, K_2' - K_2, K_2')^2 \Big], \qquad (2)$$

where the quantum number K would represent the component of angular momentum along the symmetry axis of a symmetric top molecule ($=(h/2\pi)K$), and the summation is carried out over positive integral λ bounded above by what is considered the last important multipole moment [1]. $\sum |F_m|^2$ is listed in the table, μ, Q, Ω and Φ are the permanent dipole, quadrupole, octupole and hexadecapole moments of each molecule respectively, and $\alpha_0 = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$ is the mean molecular polarizability, with $\delta = (\alpha_\parallel - \alpha_\perp)$ as the anisotropy.

2.1. *Selection rules in* (2) *for linear molecules*

(i) $K_1 = K_1' = K_2 = K_2' = 0$.

(ii) One of λ_1 or λ_2 must be 0 or 2.

(iii) $\lambda_1 + \Delta J_1$ and $\lambda_2 + \Delta J_2$ must be even.

(iv) $\lambda_1 \geqslant |\Delta J_1|$; $\lambda_2 \geqslant |\Delta J_2|$.

The allowed ΔJ_1 and ΔJ_2 are restricted by what are taken to be the important multipole moments. If the hexadecapole (Φ) is the last important moment, the summation in (2) is over $\lambda_1 \leqslant 4$, $\lambda_2 \leqslant 4$. In this case, the allowed ΔJ_1, ΔJ_2 transitions, together with the associated allowed (λ_1, λ_2) factors lead to a summation in (2) over selected Clebsch–Gordan coefficients. The resultant

λ_1	λ_2	$\sum \lvert F_m\rvert^2$
0	1	$6\alpha_0{}^2\mu^2R^{-6}$
0	2	$15\alpha_0{}^2Q^2R^{-8}$
1	2	$\frac{20}{3}\,\delta^2\mu^2R^{-6}$
2	2	$\frac{40}{3}\,\delta^2Q^2R^{-8}$
0	3	$28\alpha_0{}^2\Omega^2R^{-10}$
2	3	$\frac{280}{9}\,\delta^2\Omega^2R^{-10}$
0	4	$45\alpha_0{}^2\Phi^2R^{-12}$
2	4	$\frac{150}{3}\,\delta^2\Phi^2R^{-12}$

The coefficients $\sum |F_m|^2$ for various (λ_1, λ_2).

equations are conveniently given as the dipole-induced dipole (R^{-6} dependent), (quadrupole-induced dipole (R^{-8}), octupole-induced dipole (R^{-10}) and hexadecapole-induced dipole (R^{-12}) terms. Note that in these equations, the anisotropy (δ dependent) terms are included. N is the molecular number density.

2.2. *Dipole-induced dipole absorption*

$$
\begin{aligned}
{}_{I}A^{\mu}{}_{J\rightarrow J+1} = \frac{4\pi^3\mu^2N^2}{3hcZ}\int_0^\infty 4\pi R^{-4}\exp\left(-U_{\mathrm{AA}}(R)/kT\right)dR \\
\times\left(1-\exp\left(-hc\bar{\nu}_1(J)/kT\right)\right)\exp\left(-E_Jhc/kT\right)\bar{\nu}_1(J) \\
\times\left(4\alpha_0{}^2(J+1)+\frac{8}{3}\,\delta^2\,\frac{(J+1)^2(J+2)}{(2J+3)}\right),
\end{aligned}
\tag{3}
$$

where $\bar{\nu}_1(J)=2B(J+1)$ and $E_J=BJ(J+1)$.

2.3. *Quadrupole-induced dipole intensity*

$$
\begin{aligned}
{}_{I}A^{Q}{}_{J\rightarrow J+2} = \frac{4\pi^3Q^2N^2}{3hcZ}\int_0^\infty 4\pi R^{-6}\exp\left(-U_{\mathrm{AA}}(R)/kT\right)dR \\
\times\left(1-\exp\left(-hc\bar{\nu}_2(J)/kT\right)\right)\exp\left(-E_Jhc/kT\right)\bar{\nu}_2(J) \\
\times\left[9\alpha_0{}^2\,\frac{(J+1)(J+2)}{(2J+3)}+\frac{18}{5}\,\delta^2\left(\frac{(J+1)(J+2)}{(2J+3)}\right)^2\right],
\end{aligned}
\tag{4}
$$

where $\bar{\nu}_2(J)=2B(2J+3)$.

2.4. *Octupole-induced dipole intensity*

$$
\begin{aligned}
{}_{I}A^{\Omega}{}_{J\rightarrow J+3} = \frac{4\pi^3\Omega^2N^2}{3hcZ}\int_0^\infty 4\pi R^{-8}\exp\left(-U_{\mathrm{AA}}(R)/kT\right)dR \\
\times\left(1-\exp\left(-hc\bar{\nu}_3(J)/kT\right)\right)\exp\left(-E_Jhc/kT\right).\ \bar{\nu}_3(J) \\
\times\left[40\alpha_0{}^2\,\frac{(J+1)(J+2)(J+3)}{(2J+3)(2J+5)}+\frac{80}{3}\,\delta^2\left(\frac{(J+1)(J+2)}{(2J+3)}\right)^2\frac{(J+3)}{(2J+5)}\right],
\end{aligned}
\tag{5}
$$

where $\bar{\nu}_3(J)=6B(J+2)$.

2.5. *Hexadecapole-induced dipole intensity*

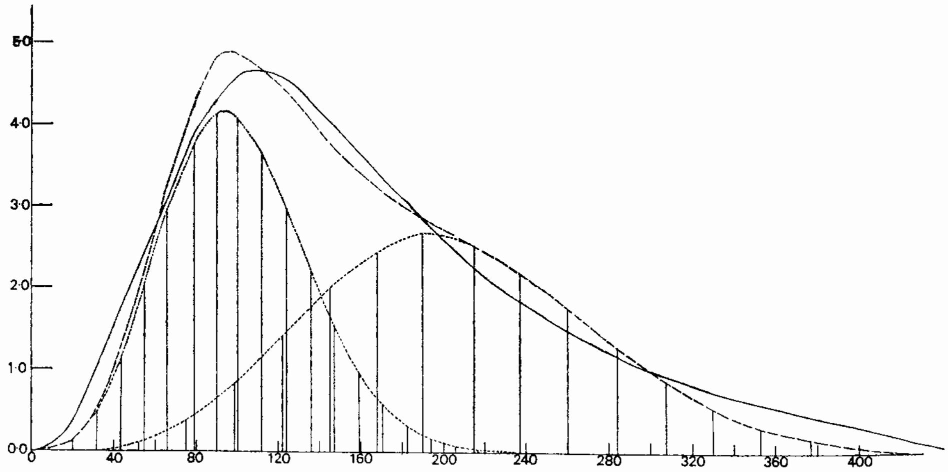
$$
{}_{l}A^{\Phi}{}_{J\to J+4}=\frac{4\pi^{3}\Phi^{2}N^{2}}{3hcZ}\int_{0}^{\infty}4\pi R^{-10}\exp\left(-U_{AA}(R)/kT\right)dR
$$
$$
\times\left(1-\exp\left(-hc\bar{\nu}_{4}(J)/kT\right)\right)\exp\left(-E_{J}hc/kT\right).\,\bar{\nu}_{4}(J)
$$
$$
\times\left[\frac{175(J+1)(J+2)(J+3)(J+4)}{2(2J+3)(2J+5)(2J+7)}\alpha_{0}^{2}\right.
$$
$$
\left.+\frac{875}{12}\delta^{2}\left(\frac{(J+1)(J+2)}{(2J+3)}\right)^{2}\frac{(J+3)(J+4)}{(2J+5)(2J+7)}\right], \quad (6)
$$

where $\bar{\nu}_4(J)=4B(2J+5)$.

3. Application

The far infra-red (10–450 cm^{-1}) spectrum (figure) of compressed oxygen gas has been observed by Bosomworth and Gush to be of exceptional breadth (160 cm^{-1} at half peak height). By comparison, the corresponding absorption [4] in compressed nitrogen is much narrower, and is fairly well simulated by the frequencies and relative intensities of the unbroadened $\Delta J=2$ rotational transitions calculated with an equation similar to (4).

Bosomworth and Gush attributed the high-frequency part of the oxygen spectrum to a short-range overlap contribution to the dipole moment, but made no quantitative analysis of the phenomenon. However, with the advent of equations (4) and (6), it is possible to simulate the oxygen band with two contributions to the bimolecular collision-induced dipole moment, assumed to arise from the quadrupole and hexadecapole moments of the field of the second oxygen molecule at the first and vice versa. (Oxygen has no dipole or octupole moment by symmetry.)



——— : Experimental (Bosomworth and Gush [4]). · · · · · · : Profiles of the $J\to J+2$ (quadrupole-induced) and $J\to J+4$ (hexadecapole-induced) dipole transitions. – – – – – : Overall theoretical profile.

Ordinate : $[\alpha(\bar{\nu})/N^2]/(\mathrm{neper\ cm^{-1}\ amagat^{-2}})$. Abscissa : $\bar{\nu}/\mathrm{cm}^{-1}$.

It is obvious that the hexadecapole field, being R^{-12} dependent, is important only at *very short* separations R. Justification for its employment in the present case comes from a simple analysis given by Bosomworth and Gush involving a rough measurement of p, the range of the induced dipole moment, which may be obtained from the width of the spectrum. Classically the spectrum is proportional to the Fourier transform of the auto-correlation function of the dipole moment ; the width being inversely proportional to that of the auto-correlation function, which is roughly equal to the duration of the collision. Thus :

$$\tau = 1/(2\pi \bar{\nu}_{1/2} c)$$

where $\bar{\nu}_{1/2}$ is the width of the spectrum at half peak height. For oxygen at 300 K, $\bar{\nu}_{1/2} = 160$ cm^{-1}, thus $\tau = 0{\cdot}1$ ps. Then p can be estimated by multiplying the duration of collision (τ) by the average rate of change of the intermolecular distance ($\dot{R}_{\mathrm{AV}}$).

Now $\frac{1}{2} m \dot{R}_{\mathrm{AV}}{}^2 = \frac{1}{2} kT$, where m is the reduced mass of the colliding molecules. Thus $p = \dot{R}_{\mathrm{AV}}\ \tau = 0{\cdot}055$ nm at 300 K. The Lennard-Jones diameter (σ) of an oxygen–oxygen pair [6] is 0·792 nm ; thus the range of the induced dipole is about $\sigma/16$. The conclusion is the same as that of Bosomworth and Gush for neon–argon pairs—the induced dipole moment is practically zero until the colliding O_2 molecules enter the repulsive region of the intermolecular potential, and rises rapidly as the molecules interpenetrate. Thus, only collisions in which the impact diameter is less than σ contribute to the absorption, i.e. very short-range fields such as the hexadecapole are expected, on this picture, to contribute significantly to the dipole-inducing process in that short interval of time when the two molecules are approaching and coming away from their point of greatest overlap. In other words, the high-frequency wing arises from the absorption of the dipole moment induced in the temporary O_2–O_2 pairs.

4. ESTIMATION OF $|Q|$ AND $|\Phi|$

Approximate values of $|Q|$ and $|\Phi|$ for oxygen can be estimated (see figure) by resolving the overall oxygen profile into a quadrupole-induced and hexadecapole-induced dipole absorption band. These are based on the line spectra calculated from the even J values in equations (4) and (6) respectively (oxygen having no odd-J contributions due to nuclear spin statistics). The considerable broadening of each line expected in practice might lead to a different overall profile than that suggested by the line spectrum alone ; nevertheless the agreement between the experimental and overall profiles is quite good, bearing in mind the experimental uncertainty.

By summing (4) and (6) over even J, and by comparison with the resolved areas, values of $|Q|$ and $|\Phi|$ can be determined. The integrals in (4) and (6) were evaluated using the tables of Buckingham and Pople [7] with Lennard-Jones parameters [6] $\epsilon/k = 118$ K, $\sigma = 0{\cdot}346$ nm for the O_2 molecule. The other constants used were [4, 8]

$$B = 1{\cdot}45 \text{ cm}^{-1}, \quad \alpha_0 = 1{\cdot}60 \times 10^{-24} \text{ cm}^3, \quad \delta = 1{\cdot}14 \times 10^{-24} \text{ cm}^3.$$

Thus :

$$\Big(\sum_{2nJ} {}_{l}A^{Q}{}_{J\to J+2}\Big) = 3{\cdot}61 \times 10^{-5}\, N^2 Q^2 \text{ neper cm}^{-2} \text{ amagat}^{-2}, \qquad (7)$$

$$\sum_{2nJ} {}_lA^{\Phi}{}_{J\to J+4}) = 4\cdot 51\times 10^{-5}\ N^2\Phi^2 \text{ neper cm}^{-2}\text{ amagat}^{-2}, \tag{8}$$

$$\left(\int_0^{\infty} \frac{\alpha(\bar{\nu})\,d\bar{\nu}}{N^2}\right)_{\text{exptl}} = 8\cdot 65\times 10^{-5}\text{ neper cm}^{-2}\text{ amagat}^{-2}.$$

Summing the left-hand side of (7) and (8) on a computer, it is found that the values of $|Q|$ and $|\Phi|$ which give best agreement with the experimental lineshape and intensity are

$$|Q| = 1\cdot 0\times 10^{-40}\text{ C m}^2,\quad |\Phi| = 3\cdot 7\times 10^{-60}\text{ C m}^4.$$

The value of $|Q|$ found compares favourably with that of $-1\cdot 34\times 10^{-40}$ C m^2 found by the induced birefringence technique [7], and $|\Phi|$ is of the correct order of magnitude, which is all that can be expected of a rough estimate such as this.

The hexadecapole moment (Φ) is one representation of the (O_2–O_2) interaction, but other data have been discussed in terms of transitory O_4 formation—these being doubtless alternative expressions of the same condition. The spectroscopic data strongly imply the hexadecapole origin of the observed higher frequency absorption in terms of the latter : nothing beyond quadrupole and hexadecapole interaction appears necessary to account for the far infra-red observations. Nevertheless, one should perhaps allow that other aspects or other models could be significantly involved in the total (O_2–O_2) interaction.

One of these is undoubtedly the angle dependent overlap interaction at very small intermolecular separations. Van Kranendonk has developed [11–13] the theory of the integrated collision-induced absorption in diatomic homonuclear molecules taking the overlap interaction ($\xi \exp(-R/p)$, where ξ is the strength of the induced dipole, R the intermolecular separation, and p the range of the induced dipole) into account. He found it [12] to be quite small compared with quadrupole induction for H_2. Ho *et al.* [14], in their detailed study of pressure-induced absorption in CO_2(g), estimated both the hexadecapole-induced dipole and overlap dipole contribution to the overall absorption intensity to be of the order of 1 per cent. However, their conclusion was reached using an arbitrary value for the hexadecapole of CO_2 and values of ξ and p for H_2, those for CO_2 being unknown. Since the high-frequency wing is so much more enhanced in O_2, it is reasonable to assume that the hexadecapole-induced contribution will be relatively more important in this latter case. A complete treatment of the O_2 absorption would have to include in addition :

(i) the overlap dipole contribution (needing good values of ξ and p) ;

(ii) translational and rotational contributions [14] of the interference between the quadrupolar and overlap induction ; and of the hexadecapole and overlap induction ;

(iii) the pure translational ($\Delta J_1 = \Delta J_2 = 0$) contribution which in the case of O_2 is hidden [4] beneath the main translational–rotational band.

Appendix

Those Clebsch–Gordan coefficients not available in the literature [8] and which have been used in deriving (5) and (6) are given below :

$$C(j_1 3j\,;\ m_1 0m) = \left[\frac{5(j_1+m+3)(j_1+m+2)(j_1+m+1)(j_1-m+3)(j_1-m+2)(j_1-m+1)}{(j_1+2)(j_1+3)(2j_1+1)(2j_1+2)(2j_1+3)(2j_1+5)}\right]^{1/2},$$

$$C(j_1 4j\,;\; m_1 0m)=\left[\frac{35(j_1+m+4)(j_1+m+3)(j_1+m+2)(j_1+m+1)\,(j_1-m+4)(j_1-m+3)(j_1-m+2)(j_1-m+1)}{8(2j_1+1)(j_1+1)(2j_1+3)(j_1+2)(2j_1+5)(j_1+3)\times(2j_1+7)(j_1+4)}\right]^{1/2}.$$

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