

ON THE DETERMINATION OF THE QUADRUPOLE MOMENT OF OXYGEN FROM SELF-BROADENED LINE WIDTHS IN THE MICROWAVE SPECTRUM*

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Abstract—The large discrepancy between the value $0.4 \text{ D } \text{\AA}$ measured by Buckingham for the quadrupole moment of oxygen and the recent value $1.21 \text{ D } \text{\AA}$ used by Yamamoto and Cattani and by Bouanich in line-broadening calculations is examined. When hexadecapolar and repulsive interactions are included, the discrepancy in the values of the quadrupole moment obtained by the bi-refringence method and line width calculations is resolved provided a value of $\Phi \sim 8 \text{ D } \text{\AA}^3$ is used for the hexadecapole moment of oxygen.

INTRODUCTION

OUR AIM in this paper is to show that the quadrupole moment of oxygen does not have to be as large as $1.21 \text{ D } \text{\AA}$ deduced recently by YAMAMOTO and CATTANI,⁽¹⁾ and by BOUANICH,⁽²⁾ in order to obtain good agreement between experimental and theoretical data for the self-broadened line widths of oxygen in the microwave⁽¹⁾ and for the oxygen-broadened line widths of carbon monoxide.⁽²⁾ The problem of calculating the latter has already been discussed, in considerable detail, elsewhere.⁽³⁾ Therefore, we need only note here that the values used for the quadrupole and hexadecapole moments of oxygen in Ref. (3) are indeed the same as those considered in the present paper. The value of $\theta(\text{O}_2) = 1.21 \text{ D } \text{\AA}$ is three times as large as the value $0.4 \text{ D } \text{\AA}$ reported by BUCKINGHAM⁽³⁾ and much larger than any of the values considered reliable by STOGRYN and STOGRYN⁽⁵⁾ among all of the available estimates for this constant. The value obtained by MURPHY and BOGGS⁽⁶⁾ is $0.58 \text{ D } \text{\AA}$ and not $1.16 \text{ D } \text{\AA}$, as has been wrongly quoted in Ref. (1). The quadrupole moment defined in Ref. (6) is twice that defined in Refs. (4) and (5) and employed in Refs. (1-3), and in the present paper.

Our line width computations are performed under the premise that the quadrupole moment of oxygen is known and is equal to the value $0.4 \text{ D } \text{\AA}$ measured by BUCKINGHAM.⁽⁴⁾ The computation is based upon an expanded version⁽³⁾ of ANDERSON-TSAO-CURNUTTE theory⁽⁷⁾ which includes terms in the interruption function due to the hexadecapole moment of oxygen and due to an empirical anisotropic repulsive force. Although our treatment of the quadrupole-hexadecapole, hexadecapole-quadrupole, hexadecapole-hexadecapole and of the repulsive forces is approximate, the main thrust of our calculation is to argue that the value $0.4 \text{ D } \text{\AA}$ for the quadrupole moment of oxygen is consistent with a calculation similar to that of YAMAMOTO and CATTANI⁽¹⁾ and of BOUANICH,⁽²⁾ that is, we wish to demonstrate that by not considering these additional interactions of much shorter range, which are

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important for a homopolar molecule with a low quadrupole moment like oxygen, Yamamoto and Cattani, and Bouanich, were led into arriving at excessively large estimates for the quadrupole moment.

CALCULATION OF LINE WIDTHS

The total interruption function in O_2-O_2 collisions is given by^(1,3)

$$S_2(b) = [S_2(b)]_{\theta\theta} + [S_2(b)]_{\theta\Phi+\Phi\theta} + [S_2(b)]_{\Phi\Phi} + [S_2(b)]_{\text{DISP+REP}}, \quad (1)$$

where

$$[S_2(b)]_{\theta\theta} = \frac{16}{25} \left(\frac{\theta^2}{\hbar v} \right)^2 \frac{1}{b^8} \left[2 \sum_{K'K_2'} Q(K, K') Q(K_2, K_2') f_3(k) + B' \sum_{K_2'} Q(K_2, K_2') f_3(k) \right], \quad (2)$$

$$\begin{aligned} [S_2(b)]_{\theta\Phi+\Phi\theta} &= \frac{256}{189} \left(\frac{\theta\Phi}{\hbar v} \right)^2 \frac{1}{b^{12}} \left[2 \sum_{K'K_2'} Q(K, K') H(K_2, K_2') f_5(k) = B' \sum_{K_2'} H(K_2, K_2') f_5(k) \right. \\ &\quad \left. + 2 \sum_{K'K_2'} H(K, K') Q(K_2, K_2') f_5(k) + B'' \sum_{K_2'} Q(K_2, K_2') f_5(k) \right], \end{aligned} \quad (3)$$

$$[S_2(b)]_{\Phi\Phi} = \frac{1024}{81} \left(\frac{\Phi^2}{\hbar v} \right)^2 \frac{1}{b^{16}} \left[2 \sum_{K'K_2'} H(K, K') H(K_2, K_2') f_7(k) + B'' \sum_{K_2'} H(K_2, K_2') f_7(k) \right], \quad (4)$$

$$\begin{aligned} [S_2(b)]_{\text{DISP+REP}} &= \frac{189\pi^2}{40960} \left(\frac{U\alpha^2\gamma}{\hbar v} \right)^2 \frac{1}{b^{10}} \left[2 \sum_{K'} Q(K, K') g_1(k) + B' g_1(0) \right] \\ &\quad - \frac{189\pi^2}{5120} \frac{U\alpha^2\gamma^2\varepsilon\sigma^{12}}{(\hbar v)^2} \frac{1}{b^{16}} \left[2 \sum_{K'} Q(K, K') g_{6-12P_2}(k) + B' g_{6-12P_2}(0) \right] \\ &\quad + \frac{48951\pi^2}{655360} \left(\frac{\gamma\varepsilon\sigma^{12}}{\hbar v} \right)^2 \frac{1}{b^{22}} \left[2 \sum_{K'} Q(K, K') g_{12P_2}(k) + B' g_{12P_2}(0) \right]. \end{aligned} \quad (5)$$

In the above equations, θ and Φ are the quadrupole and hexadecapole moments, respectively, of the oxygen molecule as defined in Ref. (5); $\alpha = (\alpha_{||} + 2\alpha_{\perp})/3$ is the mean polarizability and $\gamma \equiv (\alpha_{||} - \alpha_{\perp})/3\alpha$ is the anisotropy of polarizability in terms of the components $\alpha_{||}$ and α_{\perp} of polarizability that are parallel and perpendicular, respectively, to the internuclear axis of the molecule; U is the ionization potential; ε and σ are the Lennard-Jones parameters which have entered into equation (5) through the following empirical expression for the repulsive potential:

$$V_{REP}(R) = 4\varepsilon \left(\frac{\sigma}{R} \right)^{12} [1 + \gamma P_2(\cos \theta) + \dots], \quad (6)$$

where R and θ denote, respectively, the intermolecular separation and the angle between R and the internuclear axis of the absorbing molecule; γ is an anisotropy parameter assumed to be the same as the anisotropy of (dispersive) polarizability; $P_2(\cos \theta)$ is the second degree Legendre polynomial; $Q(K, K')$ and $H(K, K')$ are the quadrupolar and hexadecapolar transition-probabilities, which are equal to the Clebsch-Gordon coefficients $(K200|K'0)$ and $(K400|K'0)$, respectively. The impact parameter b and the mean relative velocity of collision v , which is set equal to the mean thermal speed defined in terms of the reduced mol. wt M of the colliding pair, adequately describe⁽⁷⁾ the straight-line collision-trajectory employed in the derivation of equations (2)–(5). The quantities B' and B'' are defined as

$$B' = 2(2J_i + 1)W^2(KJ_i KJ_i; 12)(2K + 1)^2 Q(K, K) W(KKKK; 12)$$

and

$$B'' = 2(2J_i + 1)W^2(KJ_i KJ_i; 14)(2K + 1)^2 H(K, K)W(KKKK; 14),$$

where W represents the Racah coefficients. The functions $f_3(k)$ and $g_1(k)$ are the same as those given in equations (162) and (161), respectively, of Ref. (7). The function $f_5(k)$ is given by TEJWANI and VARANASI.⁽⁸⁾ The functions $f_7(k)$, $g_{6-12P_2}(k)$ and $g_{12P_2}(k)$ are taken from Ref. (3) and are given below:

$$\begin{aligned} f_7(k) &= (2^7 7!)^{-2} k^{16} [K_8^2 + 16K_7^2 + 120K_6^2 + 560K_5^2 + 1820K_4^2 + 4368K_3^2 \\ &\quad + 8008K_2^2 + 11440K_1^2 + 6435K_0^2], \\ g_{6-12P_2}(k) &= \frac{\exp(-2k)}{45360} [2k^9 + 36k^8 + 330k^7 + 1974k^6 + 8343k^5 \\ &\quad + 25560k^4 + 56700k^3 + 88830k^2 + 90720k + 45360], \\ g_{12P_2}(k) &= \frac{\exp(-2k)}{33041925} [2k^{12} + 60k^{11} + 912k^{10} + 9210k^9 \\ &\quad + 68445k^8 + 393120k^7 + 1786680k^6 + 6467580k^5 \\ &\quad + 18474750k^4 + 40483800k^3 + 64297800k^2 + 66083850k + 33041925]. \end{aligned}$$

The functions $K_n(k)$ are modified Bessel functions [see Appendix C of Ref. (7)] and k is the energy exchange parameter defined by $k \equiv (b/\hbar v) \Delta E$, where ΔE is the net rotational energy exchanged in a collision.

The half-width of a microwave transition* of oxygen identified by the quantum number K is given by

$$\gamma^\circ = (n\bar{v}/2) \sum_{K_2} \rho_{K_2} b_0^2 \cdot [1 + S_2'(b_0)].$$

Here γ° refers to the half-width given in MHz per torr; n is the number density of oxygen molecules at one Torr; ρ_{K_2} is the fractional Boltzmann population of level K_2 of the perturbers; b_0 is the value of b when $S_2(b) = 1$; $S_2'(b_0)$ is obtained by replacing in the $S_2(b)$ sums appearing in equations (1)–(5), b by b_0 , $f_n(k)$ by $F_n(k_0)$, and $g_n(k)$ by $G_n(k_0)$. The functions $F_3(k_0)$, $F_5(k_0)$ and $G_1(k_0)$ may be found in Refs. (7–9). The other three functions are $F_7(k_0)$, $G_{6-12P_2}(k_0)$ and $G_{12P_2}(k_0)$ which are given below:

$$\begin{aligned} F_7(k_0) &= (2^7 7!)^{-2} k_0^{16} [K_9 K_7 + 16K_8 K_6 + 120K_7 K_5 + 560K_6 K_4 \\ &\quad + 1820K_5 K_3 + 4368K_4 K_2 + 8008K_3 K_1 + 11440K_2 K_0 \\ &\quad - K_8^2 - 16K_7^2 - 120K_6^2 - 560K_5^2 - 1820K_4^2 - 4368K_3^2 \\ &\quad - 8008K_2^2 - 5005K_1^2 - 6435K_0^2], \\ G_{6-12P_2}(k_0) &= \frac{\exp(-2k_0)}{45360} [2k_0^8 + 30k_0^7 + 225k_0^6 + 1074k_0^5 \\ &\quad + 3510k_0^4 + 8010k_0^3 + 12645k_0^2 + 12960k_0 + 6480] \\ G_{12P_2}(k_0) &= \frac{\exp(-2k_0)}{66083850} [4k_0^{11} + 102k_0^{10} + 1314k_0^9 + 11193k_0^8 \\ &\quad + 69732k_0^7 + 332982k_0^6 + 1242486k_0^5 + 3616515k_0^4 \\ &\quad + 8017380k_0^3 + 12819870k_0^2 + 13216770k_0 + 6608385]. \end{aligned}$$

* No distinction is made between K_+ and K_- transitions as the theoretical half-widths in the two cases differ by a negligible amount.

The following values are used for the various molecular constants in the line width computation. $\theta = 0.4 \text{ D } \text{\AA}$ is the value of the quadrupole moment of oxygen measured by BUCKINGHAM.⁽⁴⁾ In Ref. (3), two values for the hexadecapole moment Φ of oxygen were found to yield 'best' agreement with experimental half-width data for O_2 -broadened CO lines. A value of $\Phi_{\text{O}_2} = 7.0 \text{ D } \text{\AA}^3$ was required when a value⁽²⁾ of $\Omega_{\text{CO}} = 4 \text{ D } \text{\AA}^2$ was used for the octopole moment of CO. By taking the octopole moment of CO to be zero, it was found that $\Phi_{\text{O}_2} = 9 \text{ D } \text{\AA}^3$ would be a 'good' value. We believe⁽³⁾ that the octopole moment of CO cannot be as large as $4 \text{ D } \text{\AA}^2$ and a value closer to zero would be more realistic. Thus, it seems appropriate to use a value $6 \text{ D } \text{\AA}^3$ for the hexadecapole moment of O_2 in the present calculation. A calculation has also been made using the value $7 \text{ D } \text{\AA}^3$. The rotational constants for O_2 are taken from HERZBERG,⁽¹⁰⁾ the ionization potential is from Ref. (11) and all of the other molecular constants are from Ref. (12).

DISCUSSION OF RESULTS

The results of our line width computation are compared in Fig. 1 with the experimental data of BATTAGLIA and CATTANI⁽¹³⁾ and with the half-widths calculated by YAMAMOTO and CATTANI.⁽¹⁾ It is important to note that our results are within the experimental errors, which are 7% for $K \pm = 1, 3, 17, 19$ and 21, and 5% for the remaining lines. This observation

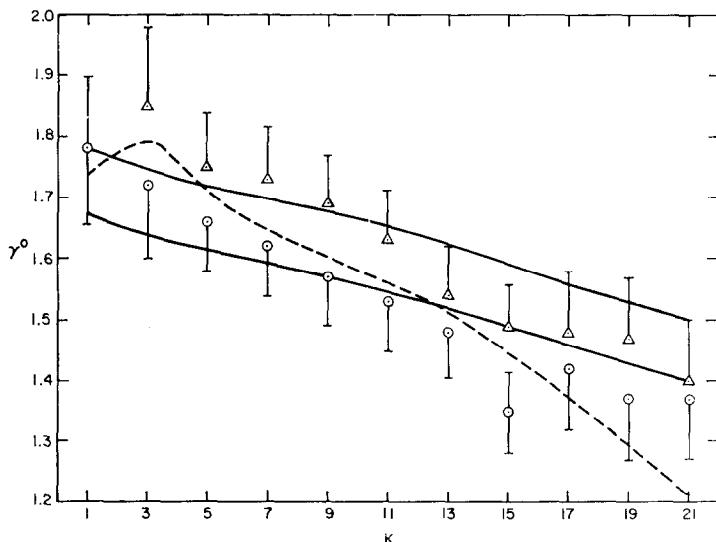


Fig. 1. Self-broadened line widths, $\gamma^\circ(\text{MHz.torr}^{-1})$, in the microwave spectrum of oxygen. Solid curves represent present calculation with $\Phi = 8 \text{ D } \text{\AA}^3$ (Bottom curve) and $\Phi = 9 \text{ D } \text{\AA}^3$ (Top curve). Dotted curve is the calculation of YAMAMOTO and CATTANI.⁽¹⁾ Circles (+ transitions) and triangles (— transitions) denote the experimental data of BATTAGLIA and CATTANI.⁽¹³⁾

when coupled with the irreconcilable fact that the interactions involving the hexadecapole moment of oxygen, whatever its value may be, cannot be ignored, convinces us that the value $1.21 \text{ D } \text{\AA}$ for the quadrupole moment used in Refs. (1) and (2) is unrealistic. Since oxygen is a homopolar molecule with an apparently low quadrupole moment of $0.4 \text{ D } \text{\AA}$, the computed half-widths are more sensitive to the value of the hexadecapole moment than to the quadrupole moment. Therefore, it can be argued that we cannot draw any definitive conclusions on the actual value of the quadrupole moment. Thus, our main concern in the

present paper has been not so much as to 'determine' a suitable value for the quadrupole moment of oxygen but to advance the view-point that BUCKINGHAM'S measured value⁽⁴⁾ can indeed be used in the line width computation. The value $8 \text{ D } \text{\AA}^3$ for the hexadecapole moment of oxygen used by us may be considered an upper bound since the trajectories in short-range hexadecapolar interactions are treated in an asymptotic manner.⁽³⁾

As is shown in Fig. 1, YAMAMOTO and CATTANI⁽¹⁾ calculated a smaller half-width for $K = 1$ transition than for $K = 3$ transition. Neither the experimental data nor our calculations exhibit this behavior. Therefore, we have repeated the calculation of Yamamoto and Cattani in our laboratory by dropping the hexadecapole and repulsive contributions from equation (1). We found the result in Ref. (1) for $K = 1$ to be in error.

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