Theoretical analysis of the collision-induced electronic absorptions in O$_2$–N$_2$ and O$_2$–CO$_2$ pairs

R.H. Tipping$^{a,*}$, Q. Ma$^b$, C. Boulet$^c$, J.-M. Hartmann$^c$

$^a$Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487, USA
$^b$Department of Applied Physics, Columbia University, and Institute for Space Studies, Goddard Space Flight Center, 2880 Broadway, New York, NY 10025, USA
$^c$Laboratoire de Photophysique Moléculaire, CNRS, Université de Paris-Sud, Centre d’Orsay, Bât 350, 91405, Orsay Cedex, France

Abstract

Theoretical calculations are made for the collision-induced electronic absorption in the atmospheric infrared $a \rightarrow X(0,0)$ and visible $b \rightarrow X(0,0)$ bands of oxygen in O$_2$–N$_2$ and O$_2$–CO$_2$ pairs. We consider only the long-range quadrupolar induction mechanism and use ab initio values for the quadrupole transition matrix elements that arise from spin-orbit mixing. By fitting the experimental value for the $a \rightarrow X(0,0)$ absorption in O$_2$–N$_2$, we obtain estimates for the isotropic and anisotropic polarizability electronic transition matrix elements of O$_2$. As a check, we then use these results together with other known data to calculate the corresponding absorption for O$_2$–CO$_2$. We find good agreement, considering experimental error and theoretical approximations. We then estimate the corresponding absorption for the $b \rightarrow X(0,0)$ absorption in O$_2$–N$_2$. We discuss briefly the observed collision-induced absorption by O$_2$–O$_2$ pairs, and conclude that there must be other induction mechanisms involved for this system. Because of the importance of absorption by O$_2$ in the Earth’s atmosphere, we conclude that a systematic study, including both additional measurements and theoretical analyses must be carried out before a satisfactory understanding can be attained.

$^*$ Corresponding author. Tel.: +1 205 348 5050; fax: +1 205 348 5051. E-mail address: rtipping@bama.ua.edu (R.H. Tipping).

Keywords: Collision-induced absorption; Molecular oxygen; Atmospheric bands

1. Introduction

The collision-induced absorption in oxygen is important from an historical as well as a practical viewpoint. Historically, collision-induced absorption (CIA) was first observed by Welsh and co-workers in the fundamental band of compressed O$_2$ in 1949 [1]. Not long after, similar absorptions were observed in the near-IR and visible regions [2]. The well-known infrared atmospheric bands ($a \rightarrow X$) and visible atmospheric bands ($b \rightarrow X$) also have allowed magnetic dipole transitions that complicate the absorption at low (1 amagat or lower) densities; however, the intensities of these allowed transitions are independent of the perturber density and scale linearly with the O$_2$ density. In contrast, the CIA scales with the product of the densities, so that at high densities, the CIA dominates [3]. Both types of absorption are important in the Earth’s atmosphere [4–6]. One also observes higher frequency double electronic transitions, in which both molecules in a colliding pair make an electronic transition that may be accompanied by vibration transitions. These absorptions are due totally to CIA because the transition operator (a collision-induced dipole) must depend on the electronic properties of both molecules, and the resulting transitions appear at the sum of the frequencies corresponding to the single transitions.

Recently, Lafferty and co-workers [7,8] have carried out accurate experimental measurements for O$_2$–N$_2$, O$_2$–O$_2$ and O$_2$–CO$_2$ in the 1.27 $\mu$m region corresponding to the $a \rightarrow X(v'=0)$ band for a range of densities and temperatures. These results allow one to separate the allowed magnetic dipole and CIA contributions, and to accurately model the corresponding absorptions for atmospheric conditions. Impelled by this work, Tipping et al. [9] have shown that
the theoretical mechanism responsible for the absorption is the quadrupole-induced dipole, where the electronic quadrupole transition moment arises from spin-orbit mixing of the low-lying electronic states. In this work, they used an old ab initio value for the quadrupole transition matrix element \((2.09 \times 10^{-2} e a_0^2)\) [10] and neglected the contribution from the isotopic and anisotropic electronic polarizability matrix elements. Thus, those theoretical values are lower limits for the absorption. Because of experimental errors and uncertainties in the accuracy of other parameters needed in the theoretical calculations, it was felt that introducing other (free) parameters to improve the agreement between theory and experiment was not warranted.

In the present paper, we present refined theoretical calculations for the \(a \rightarrow X (0,0)\) band for \(O_2–N_2\) and \(O_2–CO_2\) mixtures using the more recent ab initio transition quadrupole matrix element \((1.35 \times 10^{-2} e a_0^2)\) [11], and include contributions from the electronic polarizability matrix elements. The paper is organized as follows: in Section 2, we give a brief outline of the theory for the collision-induced absorption in electronic transitions. We then apply these results in Section 3, first to \(O_2–N_2\), neglecting any contribution from the electronic polarizability transition matrix elements; then, by fitting the experimental intensity, we obtain estimated values for the polarizability matrix elements. Using these values, we then calculate the intensity for \(O_2–CO_2\) to compare with the experimental value. We also extend the theoretical calculations to the \(b \rightarrow X (0,0)\) band for which the CIA is smaller, but not negligible for atmospheric measurements [12]. In Section 4, we discuss briefly the case of \(O_2–O_2\), where the experimental results obtained [7] are much larger than those of \(O_2–N_2\) and the theoretical estimates. Finally, we speculate on some possible reasons for this difference, and stress the need for a systematic theoretical study for CIA in \(O_2–O_2\) pairs.

### 2. Theory

The theory for the isotropic and anisotropic quadrupolar contribution to the binary absorption coefficient has been published previously, so only the relevant results will be given here. The integrated intensity \(I\) in units of \(\text{cm}^{-2} \text{atom}^{-1}\) is given by

\[
I = \frac{\int \alpha(\omega) \, d\omega}{\rho P} = 4\pi^2 \alpha Q_0^{12} f(6) \{[0 | \alpha_p | 0]^2 [\gamma | Q | X]^2 + [0 | Q_p | 0]^2 \}
\times \{[f | \alpha | X]^2 \sigma_{\text{iso}} + 2/[0 | \gamma_p | 0]^2 [\gamma | Q | X]^2 + 2/[0 | Q_p | 0]^2 [\gamma | Q | X]^2 - 4/15[0 | Q_p | 0][\gamma | Q | X]
\times [0 | \gamma_p | 0][f | \gamma | X]\sigma_{\text{aniso}}\},
\]

where \(\alpha(\omega)\) is the absorption coefficient at frequency \(\omega\) in \(\text{cm}^{-1}\) and \(\rho\) is the number density; the subscript \(P\) denotes the perturber (either \(N_2\) or \(CO_2\)). The constants \(\alpha_p\), \(n_p\), and \(\alpha_0\) are the fine-structure constant, the number density at normal temperature and pressure, and the Bohr radius. \(Q\) is the quadrupolar operator, and \(\alpha\) and \(\gamma\) are the isotropic and anisotropic polarizabilities, respectively. The ground state \(X^2^S\) for the oxygen molecule is labeled \(|X\rangle\), while the excited electronic state \(|\gamma\rangle\) is either \(a^1D_{\gamma}\) or \(b^1S_{\gamma}^+\). For the perturber, we assume \(\nu = 0\) and neglect the small rotational effects for the matrix elements. \(I(6)\) is the dimensionless integral arising from the averaging over the separation between the centers of mass \(R\)

\[
I(6) = 4\pi \int_0^\infty \exp\left[-V_{\text{iso}}(x)/kT\right] x^{-6} \, dx,
\]

where \(x \equiv R/a_0\), and we have approximated the pair distribution function by the classical limit, \(\exp(-V_{\text{iso}}(x)/kT)\), where \(V_{\text{iso}}(x)\) is the isotropic interaction potential between \(O_2\) and \(P\). For our calculations we assume a Lennard–Jones model and the parameters used are given in Table 1. The factors \(\omega_{\text{iso}}\) and \(\omega_{\text{aniso}}\) are the intensity-weighted transition frequencies [9] that are close to the band-center frequencies. The values used are also listed in Table 1.

In our previous paper [9], we used the ab initio value for the quadrupole transition matrix \(2.09 \times 10^{-2} e a_0^2\) from Mineev [10] and assumed that \(|\gamma|X\rangle\) and \(|\gamma|X\rangle\) in Eq. (1) were zero. We obtained values for \(I\) for \(O_2–CO_2\) that were in agreement with the experimental result of Fraser and Lafferty [8]; however, the theoretical value for \(O_2–N_2\) was higher than the experimental value [7] by

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Molecule</th>
<th>(O_2)</th>
<th>(N_2)</th>
<th>(CO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma(\alpha_0))</td>
<td>6.55(^a)</td>
<td>6.956(^b)</td>
<td>7.842(^c)</td>
<td></td>
</tr>
<tr>
<td>(c/k) (K)</td>
<td>106.7(^a)</td>
<td>91.5(^b)</td>
<td>190(^c)</td>
<td></td>
</tr>
<tr>
<td>(</td>
<td>0</td>
<td>\alpha_p</td>
<td>0\rangle\langle 0</td>
<td>)</td>
</tr>
<tr>
<td>(</td>
<td>0</td>
<td>\gamma_p</td>
<td>0\rangle\langle 0</td>
<td>)</td>
</tr>
<tr>
<td>(</td>
<td>0</td>
<td>Q_p</td>
<td>0\rangle\langle 0</td>
<td>)</td>
</tr>
<tr>
<td>(</td>
<td>0</td>
<td>Q_p</td>
<td>0\rangle\langle 0</td>
<td>)</td>
</tr>
<tr>
<td>(</td>
<td>0</td>
<td>Q_p</td>
<td>0\rangle\langle 0</td>
<td>)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System</th>
<th>(O_2–N_2)</th>
<th>(O_2–CO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma(\alpha_0))</td>
<td>6.753</td>
<td>7.196</td>
</tr>
<tr>
<td>(c/k) (K)</td>
<td>98.8</td>
<td>142.4</td>
</tr>
<tr>
<td>(\omega_{\text{iso}} a \rightarrow X)</td>
<td>7885</td>
<td>7885</td>
</tr>
<tr>
<td>(\omega_{\text{iso}} b \rightarrow X)</td>
<td>13121</td>
<td>13121</td>
</tr>
<tr>
<td>(\omega_{\text{aniso}} a \rightarrow X)</td>
<td>7892</td>
<td>7886</td>
</tr>
<tr>
<td>(\omega_{\text{aniso}} b \rightarrow X)</td>
<td>13128</td>
<td>13122</td>
</tr>
</tbody>
</table>

\(^a\) Ref. [13]. \(^b\) Ref. [14]. \(^c\) Ref. [15]. \(^d\) Ref. [16].
a factor 1.7. This was somewhat puzzling since the neglected terms in Eq. (1) should increase the theoretical intensities.

3. New theoretical calculations

We now present new results using the more recent ab initio values for \( |a\rangle |Q|X\) [11] and \( |b\rangle |Q|X\) [17] the values of which, after multiplying by the square root of the corresponding Franck–Condon factor, are given in Table 1. We first consider the case of the \( a \leftrightarrow X \) (0,0) transition in \( O_2\)–\( N_2\). Ignoring the small anisotropic terms in Eq. (1) we find that

\[
I = [4.80 \times 10^{-5} + 2.16 \times 10^{-3} |a\rangle |X\rangle^2] \text{ cm}^{-2} \text{ amagat}^{-2},
\]

which can be compared to the experimental value \( 6.79 \times 10^{-5} \) at \( T=296 \text{ K} \); we note that there is only a slight dependence on \( T \). By equating our result with the experimental value, we obtain the value for \( |a\rangle |X\rangle = 9.6 \times 10^{-2} a_0^3 \). In principle, one could obtain an experimental value from electronic Raman measurements or from ab initio calculations, but to the best of our knowledge, these are not available for comparison. If we make the reasonable assumption that the ratio \( |a\rangle |X\rangle/|a\rangle |X\rangle = 1/2, we can include the anisotropic terms and we find that \( |a\rangle |X\rangle = 9.06 a_0^3 \).

Next, we use the new quadrupole transition moment, along with these polarizability matrix elements and the other data from Table 1, to calculate \( I \) for the \( a \leftrightarrow X \) (0,0) transition in \( O_2\)–\( CO_2 \). We find that \( I = 2.70 \times 10^{-4} \text{ cm}^{-2} \text{ amagat}^{-2} \) which, considering the approximations made, is in good agreement with the experimental value \( 2.13(29) \times 10^{-4} \text{ cm}^{-2} \text{ amagat}^{-2} \). We note in passing but do not give numerical comparisons here, that using these matrix elements one also gets very good agreement for \( O_2\)–\( Ar \) at 298 K [18] and at 87 K [19]. Although the polarizability of \( Ar \) is smaller than that of \( N_2 \), the \( I(6) \) integral compensates, and their values are very similar.

We next consider the \( b \leftrightarrow X \) (0,0) transition for \( O_2\)–\( N_2 \). Neglecting the contributions from \( |b\rangle |z|X\rangle \) and \( |b\rangle |\gamma|X\rangle \) and using the data given in Table 1, we find the value \( I = 5.7 \times 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \). As expected from the smaller transition quadrupole matrix element, this value is approximately an order of magnitude smaller than the \( a \leftrightarrow X \) value. The experimental value obtained by Cho et al. [18] from measurements at high densities is \( I = 1.9 \times 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \). We note that the value for the \( a \leftrightarrow X \) (0,0) band obtained by Cho et al. is smaller than that obtained by Maté et al. [7] by almost the same factor of 3. Unless more accurate experimental measurements at lower densities are made, or accurate theoretical values for the \( b \leftrightarrow X \) polarizabilities matrix elements become available, we are unable to assess the accuracy of our theoretical result. Finally, we note that the allowed magnetic dipole transitions in the \( b \leftrightarrow X \) (0,0) band are approximately stronger by a factor of 100 compared with those in the \( a \leftrightarrow X \) (0,0) band; this means that the collision-induced absorption is relatively much less important for this band than for the \( a \leftrightarrow X \) (0,0) band.

4. Collision-induced absorption in \( O_2\)–\( O_2 \) pairs

In the discussion above, we have shown that for \( O_2 \) colliding with a different perturber such as \( N_2 \), \( CO_2 \), or Ar atoms, one can get reasonable agreement between experimental and the theoretical results by considering only the long-range quadrupolar induction mechanism, where the quadrupole transition matrix element arises from spin-orbit interaction. This is not the case for two \( O_2 \) molecules as can be seen immediately from the experimental \( a \leftrightarrow X \) (0,0) results of Maté et al. The intensity for \( O_2\)–\( O_2 \) is more than a factor of 5 greater than for \( O_2\)–\( N_2 \), whereas the polarizability matrix elements and the intermolecular potentials are comparable. Thus, the theory outlined in the previous section predicts too little absorption. Furthermore, for the single transitions to excited upper state vibrational levels, e.g. the \( a \) (\( v'=1 \)–\( v=0 \) band, the intensity does not fall off as rapidly as one would expect considering the Franck–Condon factors. For instance, Tabisz et al. [2] found for the (0,0) band \( I = 3.05 \times 10^{-4} \text{ cm}^{-2} \text{ amagat}^{-2} \) (close to that of Maté) while for the \( a \) (\( v'=1 \)–\( v=0 \) band, they found \( I = 2.36 \times 10^{-4} \text{ cm}^{-2} \text{ amagat}^{-2} \). Many other workers [20–22] and references therein] also found unexpected intensities for the double electronic transitions such as \( 1S_g + 1S_g \leftrightarrow X^3 \Sigma_g^- + X^3 \Sigma_g^- \). In this case, the intensity when one of the oxygen molecules makes the transition to the vibrationally excited state \( v'=1 \) state is stronger than when both molecules make purely electronic transitions. Similarly, very large enhancements for spin-forbidden transitions for \( O_2 \) in different liquid solvents have also been reported [23].

To explain the above experimental findings, several different hypotheses have been proposed. For the \( a \leftrightarrow X \) (0,1) band, Tabisz et al. [2] found that there were two contributions. The most intense is where one molecule makes both the electronic and vibrational transition, while the other molecule makes either no or only a rotational transition. The smaller contribution arises when one molecule makes the (0,0) electronic transition, while the other molecule makes a fundamental vibration–rotation transition. Because the narrowness of the latter profile, they inferred that a longer-range interaction was responsible, while for the former component, a shorter-range induced dipole was involved. This was supported by the low-temperature measurements by McKellar et al. [24]. Because of the rapid increase in the integrated intensity as the temperature decreases, they also
conjectured that a short-range exponential dipole was the main induction mechanism. Such a component, called the isotropic overlap, is well known to dominate the fundamental CIA spectrum of \( \text{H}_2 \). In fact, all the long-range multipolar components have a similar short-range exponential part. However, for the translation-rotational \([25]\) and fundamental \([26]\) CIA in \( \text{O}_2 \), such short-range effects are not very significant. Several authors have suggested that collisional mixing of electronic states can significantly alter the intensities of spin-forbidden electronic transitions \([23,27]\). This seems to be plausible, but to the best of our knowledge, no systematic calculations have been made for a comprehensive comparison between experimental and theoretical CIA intensities, although enhanced collision-induced radiative emissions have been extensively studied \([10,11,17,28,29]\).

For double electronic transitions, there are other as yet unexplained intensity anomalies. For instance, for the \( \Delta_g^1 + \Delta_g^1 \leftrightarrow X^3 \Sigma_g^+ + X^3 \Sigma_g^- \) transitions in the spectral region between 15,000 and 18,000 cm\(^{-1}\), despite the much smaller Franck–Condon factor, the (0,1) band is even stronger than the (0,0) band \([19,20]\). Part of this may be due to the symmetry requirement of the short-range isotropic overlap induced dipole. When both molecules in the pair make identical transitions, this dipole does not contribute \([30]\).

Because of the importance of the absorption of incoming sunlight by \( \text{O}_2 \), many experimental measurements have been carried out both in the laboratory and in the atmosphere. In atmospheric spectra, sharp magnetic dipole transitions can be identified and taken into account. However, the broad, featureless CIA background is very difficult to measure. As mentioned previously, this can be comparable to that of the sharp features for the \( a^+ \leftrightarrow X \) (0,0) band, and non-negligible for several other bands. This is why studies such as those made by Lafferty and co-workers \([7,8]\) that allow one to separate the allowed lines from the CIA background are very useful. They also provide accurate integrated intensities that are helpful for ascertaining the theoretical mechanisms responsible for this absorption. Before a satisfactory understanding of the absorption by \( \text{O}_2 \) in collisions with different perturbers, and with other \( \text{O}_2 \) molecules can be realized, much more theoretical and experimental work will be needed.

Acknowledgements

Two of the authors (R.H.T. and Q.M.) would like to acknowledge support from NASA through Grant No. NAG5-13337.

References