Selfshifting of CO2 lines in the 3v3 band at 1.43 μm

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+ H_2O relative to OH($X\,^2\Pi$) + NH$_2$ ($X\,^2B_1$ and $A\,^2A_1$), based
on the measured vibrational state ratios and upper limits
on NH($a\,^1\Delta$, $v>0$) and OH($X\,^2\Pi$, $v>2$), is in the range
0.03–0.15. The OH($X\,^2\Pi$) internal energy distribution
observed here is suggestive of a hydrogen abstraction
mechanism[3,4,8] dominating the formation of OH, but does
not preclude OH formation by insertion into the N–H
bond which is the likely source of the NH + H_2O channel.

Recently, Rettner, Cordova, and Kinsey[6] have pub-
lished a study of the O(^1D) + NH$_3$ reaction. Their ex-
periment differs from ours by the use of a broad pulse-
width dye laser (~1 μsec). Their observations, which
include only channels to OH($X\,^2\Pi$, $v=0,1$), indicate a
$v=1/v=0$ ratio of 0.65 in substantial disagreement with
our value.

Further work on this problem is in progress and a
more detailed exposition of the OH($X\,^2\Pi$) and NH($a\,^1\Delta$) ro-
tation–vibration distributions using data taken under
varying conditions is anticipated.

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NOTES

Self-shifting of CO$_2$ lines in the 3ν_3 band at 1.43 μm

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In a study[1] of the absorption bands of CO$_2$ at 1.43 μm
using the high resolution Fourier transform spectrom-
eter at Meudon, we have found a systematic negative
shift of the lines between spectra recorded at low (4
Torr) and high pressure (280 Torr). In this paper, we
present preliminary results of new experiments per-
formed at Meudon that assert the reality of these shifts
which have been always assumed negligible for CO$_2$.
In order to avoid any problem concerning the determina-
tion of line shifts from different spectra, we have used
a single beam two cells method; the light first goes
through a multiple pass cell filled with a low pressure
(4 Torr) of CO$_2$ and then through another one with a high
CO$_2$ pressure (752 Torr). The resolution of the spectra
was of 0.004 cm^{-1}, given as the half-width at half-height
of the apparatus function.

Figure 1 exhibits clearly the pressure shifts for the
$R(6)$ line. "A" is the high pressure Lorentzian line and
"B" corresponds to the low pressure line that has a
Gaussian shape under the experimental conditions. Us-
ing only the primary points of the spectra, we fit by a
least-square procedure the A component to a Lorentzian
formula, setting the weights of the points of the B part
to zero. This procedure gives us the position of the
shifted line and all the parameters necessary to subtract
the Lorentzian component from the total spectrum. We
can then measure the position of the unshifted line labelled
C on Fig. 1.

The general features of the lineshifts can be listed in
the following way: (a) For all the P and R lines in this
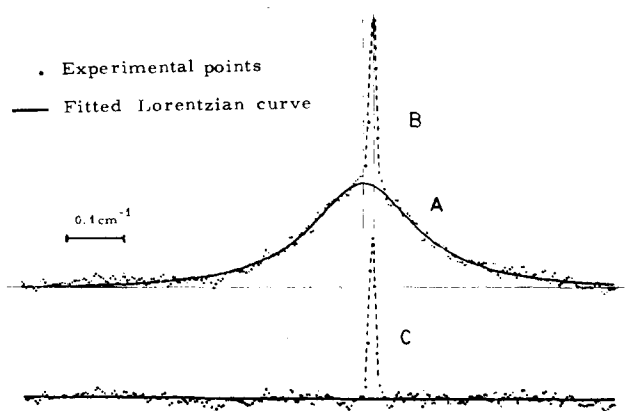band the shifts are negative with a weak J dependence

FIG. 1. Drawing of the $R(6)$ line showing the shifting of the high pressure Lorentzian line A with regard to the unshifted low pressure Gaussian one B. C represents the Gaussian line after the fitted Lorentzian curve has been subtracted from the experimental points. Dashed lines are drawn only for clarity.

which must be corroborated later. (b) The shift of the $R(6)$ line which can be considered as the mean value of the shift in this band is measured as $\delta_{f_i} = -0.014 \pm 0.004$ cm^{-1} atm^{-1}.

The general trend of the experimental data indicate that these shifts originate from a vibrational mechanism which will be now outlined. For cases in which the semi-classical and impact approximations hold, the shift δ_{f_i} of a spectral line can be written in terms of a collision efficiency function $S(b, v, j_2)$ which is given, according to the formalism recently proposed by Robert and Bonamy,[2,3] by:

$$S(b, v, j_2) = 1 - (1 - S_{2\,\text{middle}}^{ND\,\text{aniso}})\exp[-(S_{2\,\text{outer}\,f}^{\text{aniso}} + S_{2\,\text{outer}\,i}^{\text{aniso}} + S_{2\,\text{middle}}^{D\,\text{aniso}}]\exp[-iS_1^{\text{iso}}(b, v, j_2)] \,. \quad (1)$$

In this equation, all the S_2 contributions[2] are related to the anisotropic part of the intermolecular potential. On the other hand, the vibrational phase shift S_1^{iso} arises because the isotropic part of the potential has different expectation values for various vibrational states of the active molecule. The $3\nu_3$ band S_1^{iso} is given by:

$$S_1^{\text{iso}} = \hbar^{-1} \int_{-\infty}^{+\infty} dt \langle 3\nu_3 | V_{\text{iso}} | 3\nu_3 \rangle - \langle 00^00 | V_{\text{iso}} | 00^00 \rangle \,. \quad (2)$$

In this equation, $|3\nu_3\rangle$ and $|00^00\rangle$ represent, respectively, the final and initial vibrational states of a transition. In order to calculate this phase shift, the isotropic part of the *intermolecular* potential is developed in terms of the vibrational coordinates of CO_2 (q_1 refers to the symmetric stretching mode, etc....):

$$V_{\text{iso}} = V_{\text{iso}}(\text{eq}) + (\partial V_{\text{iso}}/\partial q_1) q_1 + \tfrac{1}{2}(\partial^2 V_{\text{iso}}/\partial q_1^2) q_1^2$$
$$+ \tfrac{1}{2}(\partial^2 V_{\text{iso}}/\partial q_3^2)q_3^2 + \cdots \quad (3)$$

Let us note that due to the Σ_g^+ character of the isotropic potential, the single first order contribution is proportional to q_1. This term (and the second order derivatives) can be related to the derivatives of the CO_2 polarizability, following the method used for diatomic molecules.[4] *Ab initio* derivatives of the CO_2 polarizability have recently been calculated by Morrison *et al.*[5] Therefore the calculation of the line shifts can be performed *without any adjustable parameters*.

We now consider the final vibrational state. As a result of the mixing due to the anharmonic part of the *intramolecular* potential, the wave function $|3\nu_3\rangle$ is a linear combination of the vibrational basis function[6]:

$$|3\nu_3\rangle = 0.89405|00^03\rangle + 0.40412|10^03\rangle + 0.13596|20^03\rangle. \quad (4)$$

From this equation it appears that the first order contribution $\partial V_{\text{iso}}/\partial q_1$ gives a nonvanishing contribution to the vibrational phase shift. This is by far the most important phase shift because of the very large coupling between the $|00^03\rangle$ and $|10^03\rangle$ states (c.f. Eq. 4). Indeed the second order contributions remain smaller by one order of magnitude than the first order one. Knowing the components of the vibrational states and the expressions of the intermolecular potential derivatives, the calculation of the line shifts can be performed.

The calculated shifts vary from -0.010 to -0.015 cm^{-1} atm^{-1} as $|m|$ increases from 5 to 35. It should be noted that these results are very consistent with experiments.

In summary, we have demonstrated the existence and the vibrational nature of the pressure shifts in CO_2 bands. This result suggests extending this work to the case of other vibrational bands. Studies on this aspect are being pursued further.

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