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Microwave radii in nonresonant spectra

G. Buffa and O. Tarrini

Gruppo Nazionale di Struttura della Materia, Consiglio Nazionale delle Ricerche, Sezione di Pisa, Pisa, Italy

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The microwave cross section σ for Debye-like spectra resulting from overlapping lines at high pressures is computed. The main idea is a modification of Anderson's model, by which the cross section is computed for an effective line instead of computing it for the single overlapping lines. This gives a natural explanation of the observed reduction of σ compared to σ for the isolated lines. Complete numerical calculations are carried out for the case of Debye spectra of symmetric-top molecules. Agreement with experiment is satisfactory.

I. INTRODUCTION

Microwave absorption spectra resulting from overlapping of pressure-broadened lines are usually described in terms of Lorentzian line shapes. The width Γ is given by $\Gamma = nv\sigma$ where n and v are the number density and the mean relative velocity of the molecules and σ is defined as "microwave cross section." The cross section resulting from the overlap of several lines is usually much smaller than the cross section for each of the resolved lines, as observed at lower pressure. This reduction of σ has been observed in the inversion spectra of symmetric-top molecules,[1,2] in overlapping of rotational lines of dipolar molecules,[3,4,5] in magnetic dipolar absorption of O_2[6,7] and in other cases.

In the range of pressure in which the existing measurements[1,2] fall, the assumption of impact theory,[8,9] i.e., duration of a collision is small compared to the time interval between two subsequent collisions, is satisfied, due to the smallness of the cross section. The "microwave radii" r typically are ~7 Å, and hence the ratio $R =$ (duration of a collision)/(average time between two subsequent collisions) is typically $R = \pi r^3 n \simeq 0.02p(\text{atm})$.

According to the impact theory developed by Baranger[8] the reduction of the cross section for overlapping spectral lines can be interpreted[5,10] in terms of interference in relaxation between neighboring lines of the band. One way to evaluate this interference effect in terms of intermolecular forces is to extend to overlapping lines Anderson's model,[11] which proved successful in calculating the width of isolated lines at low pressure.

As we shall discuss in Sec. II, if such extension is done in terms of low-pressure data, i.e., starting from the isolated lines, theory agrees with experiment only up to pressures at which only the wings of lines overlap. This is confirmed by the fit[12] with measured data for NH_3: at high pressure, when overlapping gives rise to a unique profile, calculated radii are larger than the measured ones.

For NH_3 and O_2 an explanation has been given by Gersten and Foley,[13] who explicitly calculated the Ben-Reuven cross relaxation terms. Unfortunately their method cannot be extended to other symmetric-top molecules, for which rotational transitions $\Delta J \neq 0$ are no more negligible.

For NH_3 an alternative explanation has been given[12] considering that the discrepancies can be caused by the failure of impact approximation. Assuming as microwave radius the 13.2-Å low-pressure radius for the isolated line, the number R measuring the validity of impact theory is of the same order of discrepancies. However, if one tries to extend this approach to the Debye spectrum of other symmetric tops, as ND_3, one is in trouble, since the Debye absorption is observed at lower pressure, where the validity of impact theory is not questionable.

In Sec. III we propose an alternative approach to the application of Anderson's theory considering the whole band as a new effective line, as suggested by the observed spectrum. In this way the cross section and the cut-off radius b_0 can be computed for this line, instead of computing them for the single overlapping lines.

In Sec. IV an explicit expression is derived for the linewidth of Debye spectrum of symmetric-top molecules interacting through dipole-dipole force. Numerical results are computed and compared with existing experimental data.

II. LINE SHAPE OF A BAND

The line shape $I(\nu)$ of a dipolar gas absorbing radiation at frequency ν, in the Liouville representation[14] is given by

$$I(\nu) = \text{Im}(\mu \,|\, \frac{1}{\nu - L} \,|\, \mu) \; ; \tag{2.1}$$

μ is the dipole moment of the absorbing molecule; the scalar product $(A|B)$ means $\text{Tr}\{\rho A^\dagger B\}$, ρ is the density matrix of the internal degrees of the absorber, and L is the non-Hermitian Liouville operator whose imaginary part describes relaxation. In the low-density limit the relaxation is linear with the number density n of the gas.

In a representation in which the isolated lines l with frequency ν_l are a basis,

$$L_{ll'}=\nu_l\delta_{ll'}+in\gamma_{ll'}. \qquad (2.2)$$

If we neglect the shift, which is small compared to the width, γ_{ll} is essentially real and $n\gamma_{ll}$ is the width of the isolated line l whose shape is a Lorentzian. At higher-pressure broadening causes neighboring lines to overlap; then mixing terms $n\gamma_{ll'}$ in the relaxation are no further negligible and the spectrum can result very modified with respect to the spectrum one would obtain by extrapolating the naive sum of the lines observed at low pressure. In many cases the entire profile can be fairly well fitted by a single Lorentzian shape with intensity I_0 and resonance ν_0, respectively, equal to the intensity and the centroid of the band. Formally, this is obtained by transferring the average on the lines contained in the scalar product $(\mu|\ldots|\mu)$ to the denominator of Eq. (2.1). Then one obtains

$$I(\nu)=I_0\frac{n\overline{\gamma}/2\pi}{(\nu-\nu_0)^2+(n\overline{\gamma}/2\pi)^2}, \qquad (2.3)$$

where the intensity factor I_0 is given by

$$I_0=\sum_l \rho_l|\mu_l|^2, \qquad (2.4)$$

the centroid of the band by

$$\nu_0=\sum_l \rho_l|\mu_l|^2\nu_l/I_0, \qquad (2.5)$$

and the "effective width" $n\overline{\gamma}$ by

$$\overline{\gamma}=\sum_{ll'} \rho_l\mu_l\gamma_{ll'}\mu_{l'}/I_0. \qquad (2.6)$$

In impact approximation

$$\gamma_{ll'}=\sum_r \rho_r v\int_0^\infty 2\pi b\,db\,P_{ll'}(b,r), \qquad (2.7)$$

where $P_{ll'}(b)$ describes the average effect of a collision with impact parameter b. In terms of the scattering matrix $T(b)=i[S(b)-1]$, we have

$$P_{ll'}(b,r)=\langle l_i,r|T(b)|l_i',r\rangle\delta_{ll'}+\langle l_f,r|T^{\dagger}(b)|l_f',r\rangle\delta_{ll'}-\sum_{r'}2\langle l_i,r|T(b)|l_i',r'\rangle\langle l_f',r'|T^{\dagger}(b)|l_f,r\rangle. \qquad (2.8)$$

Here l_i and l_f are the initial and final state for the line l and l_i', l_f' the corresponding states for l'; r and r' describe the initial and final internal state of the perturber.

By Eqs. (2.6) and (2.7) and by the unitary nature of the S matrix, $\overline{\gamma}$ can be expressed[10] in the form

$$\overline{\gamma}=\sum_r \rho_r v\int_0^\infty 2\pi b\,db\,\overline{P}(b,r), \qquad (2.9)$$

where

$$\overline{P}(b,r)=I_0^{-1}\sum_{l,l',r'}\rho_l|\mu_l\langle l_i,r|T(b)|l_i',r'\rangle -\mu_{l'}\langle l_f,r|T(b)|l_f',r'\rangle|^2. \qquad (2.10)$$

By Eq. (2.8), when the scattering matrix $T(b)$ is known, $P(b)$ can be obtained and the problem of calculating the width $n\overline{\gamma}$ is completely resolved by Eqs. (2.9) and (2.10). But a complete knowledge of $T(b)$, as pointed out by Anderson, is unnecessary.

Anderson proposed a method based on the definition of a cut-off radius b_0, such that for $b<b_0$ collisions can be considered as "strong," so that every correlation is lost and $P_{ll'}=P_{ll'}^{\text{strong}}=\delta_{ll'}$. For $b>b_0$ collisions are "weak" and interaction is treated as a perturbation which can be easily calculated assuming molecules to move following straight line paths. The cut-off radius b_0 for a fixed line l, is assumed by Anderson as the shortest radius at which the lowest-order term for $P_{ll}^{\text{weak}}(b)$ in the perturbative treatment exceeds the unitary bound, i.e., $P_{ll}^{\text{weak}}(b_0)=1$. Clearly, b_0 depends on l.

This model has been successful in calculating the width of isolated resonant lines.[15] In the next section we adapt it in order to calculate $\overline{\gamma}$. Our approach is based on treating the $\overline{P}(b)$ of Eq. (2.10) as relative to a new line vector $|\overline{l}\rangle$ describing the whole band, i.e., $\overline{P}(b)=P_{\overline{l}\overline{l}}(b)$. The cut-off radius b_0 is so calculated in this line $\overline{l}$: $P_{\overline{l}\overline{l}}(b_0)=1$.

III. DETERMINATION OF b_0

According to the physical situation, in which the spectrum exhibits a single Lorentzian shape and the individual lines are completely destroyed, we define the effective line vector $|\overline{l}\rangle$ as the sum of the individual line vectors $|l\rangle$, internal to the band, weighted with the amplitude intensity μ_l of the line, i.e.,

$$|\overline{l}\rangle=\sum_l \mu_l|l\rangle/I_0^{1/2}. \qquad (3.1)$$

In this way the intensity $|(\mu|\overline{l})|^2$ and the resonance $\mathrm{Re}(\overline{l}|L|\overline{l})$ assume the form required, respectively, by (2.4) and (2.5) relative to the Lorentzian shape describing the band.

The Anderson's cut-off radius $b_0(r)$ is so fixed by

$$P^{\text{weak}}_{\overline{ll}}(b_0(r), r) = 1\,. \tag{3.2}$$

At this point the width $\bar{\gamma} = \gamma_{\overline{ll}}$ can be expressed by

$$\bar{\gamma} = \sum_r \rho_r(\bar{\gamma}_r^{\text{strong}} + \bar{\gamma}_r^{\text{weak}})\,, \tag{3.3}$$

where

$$\bar{\gamma}_r^{\text{strong}} = \pi v b_0^2(r)\,, \tag{3.4}$$

$$\bar{\gamma}_r^{\text{weak}} = v \int_{b_0(r)}^{\infty} 2\pi b \, db \, \bar{P}^{\text{weak}}(b, r)\,. \tag{3.5}$$

In the frame of Anderson's model, our determination of b_0, always allows to select the smaller between $\bar{P}^{\text{strong}}$ and $\bar{P}^{\text{weak}}$; i.e., we minimize the cross section $\sigma = \bar{\gamma}/v$. Any other determination of b_0 causes in some interval of b to select the larger of the two. If, according to low-pressure data, one would define b_0 through $P_{ll}(b_0) = 1$, then one would obtain for the well-known spectra of NH_3 and ND_3 a width $\bar{\gamma}$ reduced for a factor $\eta \geq \frac{1}{2}$ compared to the width of the isolated inversion line. This result is straightforward considering that $\bar{\gamma}^{\text{strong}}$ is not affected by interference and that for NH_3 and ND_3 $\bar{\gamma}^{\text{weak}} = \bar{\gamma}^{\text{strong}}$.[12] The maximum possible effect of interference is so to destroy the "weak" part of the cross section, so that $\eta = \frac{1}{2}$. But this would be in complete disagreement with experience that give $\eta \simeq \frac{1}{3}$ and $\eta \simeq \frac{1}{4}$ for NH_3 and ND_3, respectively.

IV. NONRESONANT SPECTRA OF SYMMETRIC-TOP MOLECULES

We apply the method developed in the preceding section to calculate explicitly the Debye linewidth of symmetric-top molecules interacting through a force which is mainly dipole-dipole.

Denoting by J, K and J_r, K_r the rotational states of the absorber and the perturber respectively, Eqs. (3.3), (3.4), and (3.5) become

$$\bar{\gamma} = \sum_{J_r K_r} \rho_{J_r K_r}(\bar{\gamma}_{J_r K_r}^{\text{strong}} + \bar{\gamma}_{J_r K_r}^{\text{weak}})\,, \tag{4.1}$$

$$\bar{\gamma}_{J_r K_r}^{\text{strong}} = \pi v b_0^2(J_r, K_r)\,, \tag{4.2}$$

$$\bar{\gamma}_{J_r K_r}^{\text{weak}} = 2\pi v \int_{b_0(J_r, K_r)}^{\infty} b \, db \, \bar{P}^{\text{weak}}(b, J_r, K_r)\,. \tag{4.3}$$

The cut-off radius $b_0(J_r, K_r)$ is now defined by

$$\bar{P}^{\text{weak}}(b_0, J_r, K_r) = 1\,. \tag{4.4}$$

The explicit calculation of $\bar{P}^{\text{weak}}(b, J_r, K_r)$ is carried out in Appendix A. Denoting by $f_{dd}(k)$ and $F_{dd}(k)$ the functions defined by Tsao and Cornutte[16] in terms of modified Bessel functions, by J' and J'_r the final rotational quantum numbers of the absorber and the perturber, respectively, connected to J and J_r by the selection rule $\Delta J = 0, \pm 1$, and by $\hbar\Delta\omega$ the jump in the collision of the total rotational energy, the resulting expression is

$$\bar{P}^{\text{weak}}(b, J_r, K_r) = \frac{8\mu^4}{9\hbar^2 v^2 b^4} I_0^{-1} \sum_{JKJ'J'_r} \rho_{JK} |\langle J'K | 10JK \rangle|^2 |\langle J'_r K_r | 10 J_r K_r \rangle|^2 f_{dd}(b\Delta\omega/v) \frac{K^2}{J(J+1)J'(J'+1)}\,. \tag{4.5}$$

Substituting in (4.3) and integrating we obtain

$$\bar{\gamma}_{J_r K_r}^{\text{weak}} = \bar{\gamma}_{J_r K_r}^{\text{strong}} \frac{8\mu^4}{9\hbar^2 v^2 b_0^4} I_0^{-1} \sum_{JKJ'J'_r} \rho_{JK} |\langle J'K | 10JK \rangle|^2 |\langle J'_r K_r | 10 J_r K_r \rangle|^2 F_{dd}(b_0\Delta\omega/v) \frac{K^2}{J(J+1)J'(J'+1)}\,. \tag{4.6}$$

By (4.1) now the value of $\bar{\gamma}$ and the Debye width $\Delta\nu = n\bar{\gamma}/2\pi$ can be numerically computed. Comparing the expression (4.5) with the one obtained by Tsao and Cornutte for resonant lines, we note that the nonresonant expression differs essentially for the presence of a $1/J(J+1)$ factor that causes the drastic reduction of nonresonant cross section. The $\propto b^{-4}$ dependence of $\bar{P}$ gives, roughly, $\bar{\gamma} \propto \sqrt{\bar{P}}$, and so $\bar{\gamma} \propto J^{-1}$. This result agrees with the empirical law proposed by Birnbaum,[17] who measured $\bar{\gamma}$ for several symmetric-top molecules and noted that $\bar{\gamma} \propto \mu^2 \langle J^{-1} \rangle$.

If rotational transitions are disregarded it is easy to see that our expression for $\bar{\gamma}$ essentially

TABLE I. Comparison of theory with experiment.

Gas	μ (Debye)	B (GHz)	r (Å) calculated	r (Å) measured
NH_3	1.468	298	7.1	7.7[a]
ND_3	1.468	154	6.6	6.9[b]
CH_3F	1.79	25.5	7.5	6.5[c]
CH_3Cl	1.87	13.3	8.0	7.2,[c] 7.6,[d] 7.7[a]
CH_3I	1.65	7.50	7.8	8.5[c]
CH_3Br	1.80	9.57	8.1	7.8,[c] 8.825,[d] 9.0[a]
CH_3CN	3.913	9.20	13.8	12.4[c]
CHF_3	1.65	10.34	5.8	5.3[c]

[a] See Ref. 2.
[b] See Ref. 18.
[c] See Ref. 19.
[d] See Ref. 20.

reduces to the one obtained by Gersten and Foley.[13]

From (4.5) and (4.6) we have numerically computed nonresonant line width for symmetric-top molecules having large dipole moment. The resulting radii are reported in Table I and compared with experimental values. The agreement is very good if compared to the one one would obtain by the usual method discussed in Sec. III, which would give for NH_3 and ND_3 microwave radii ~10 Å, instead of the observed 7.7 and 6.9, respectively. For other molecules the discrepancy would be even greater. Other methods, such as the one proposed by Birnbaum,[1] give microwave radii ~1 Å, about one order of magnitude smaller than the measured ones.

The improvement of our method is evident.

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APPENDIX A

For nonresonant absorption in symmetric-top molecules: $l_i = l_f = JKM$; $l_i' = l_f' = J'K'M'$; $r = J_r K_r M_r$. Eq. (2.10) becomes

$$\overline{P}^{\text{weak}} = I_0^{-1} \sum_{JKJ'K'r'} \rho_{JK} \frac{1}{2J+1} \sum_{MM'} \left| \langle JKM, r \,|\, T(b) \,|\, J'K'M', r' \rangle \right|^2 \left| \mu_{JKM} - \mu_{J'K'M'} \right|^2 . \tag{A1}$$

Following Anderson, at the lowest order in the interaction V, the scattering amplitude $\langle m \,|\, T(b) \,|\, n \rangle$ for the transition $m \rightarrow n$, is given by

$$\langle m \,|\, T(b) \,|\, n \rangle = \hbar^{-1} \int_{-\infty}^{\infty} \exp(i\omega_{mn} t) \langle m \,|\, V(t) \,|\, n \rangle \, dt . \tag{A2}$$

For molecules with large dipole moment,

$$V(t) = \frac{1}{r^3(t)} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3\vec{\mu}_1 \cdot \vec{r}(t)\, \vec{\mu}_2 \cdot \vec{r}(t)}{r^2(t)} \right] . \tag{A3}$$

In Eq. (A1) the intensity I_0 and the factor $|\mu_{JKM} - \mu_{J'K'M'}|^2$, describing the variation in the collision of the orientation of the dipole moment, are defined by

$$I_0 = \sum_{JK} \rho_{JK} \mu_{JK}^2 ,$$

$$\mu_{JKM} = \mu_{JK} \langle JM \,|\, 10JM \rangle ,$$

where $\mu_{JK}^2 = K^2/J(J+1)$ and $\langle JM \,|\, 10JM \rangle$ is the usual Clebsch-Gordan coefficient.

Following Anderson the time dependence of $V(t)$ is assumed to be defined by straight classical motion. Substituting (A3) into (A2) and performing in (A1) the summation over the magnetic quantum numbers M, M', one obtains[5]:

$$\overline{P}^{\text{weak}}(b, J_r, K_r) = I_0^{-1} \frac{4\mu^4}{9\hbar^2 v^2 b^4} \sum_{JKJ'J_r'} \rho_{JK} \left| \langle J'K \,|\, 10JK \rangle \right|^2 \left| \langle J_r' K_r \,|\, 10 J_r K_r \rangle \right|^2 f_{dd}(b\Delta\omega/v)$$
$$\times \left[\mu_{JK}^2 + \mu_{J'K}^2 - 2\mu_{JK}\mu_{J'K}(2J'+1)^{1/2}(2J+1)^{1/2}(-)^{J+J'} W(JJJ'J'; 11) \right] . \tag{A4}$$

Substituting

$$\mu_{JK}^2 + \mu_{J'K}^2 - 2\mu_{JK}\mu_{J'K}(2J'+1)^{1/2}(2J+1)^{1/2}(-)^{J+J'} W(JJJ'J'; 11) = 2K^2/J(J+1)J'(J'+1) ,$$

we obtain Eq. (4.5) of text.

For other multipolar forces the calculations of $\overline{\gamma}$ is completely analogous and can be derived from Refs. 5 and 16.

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