

Nuclear-quadrupole effects in the pressure broadening of molecular lines

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We report the first experimental evidence of variable collision-broadening parameters within the hyperfine multiplet of a rotational line. A similar behavior is observed in the Stark pattern of one hyperfine line. All the experimental results, obtained on CH_3I , are explained in terms of a theoretical model accounting for line coupling. The same approach is successful in interpreting the literature data for the Stark lines of CH_3Br and previous null results for other molecules.

I. INTRODUCTION

The pressure-broadening (PB) parameters of molecular lines are receiving a growing interest. They provide important information for molecular physics and are useful in the interpretation of atmospheric and astrophysical data. In the last few years attention was particularly focused on line-coupling effects, which can be formally described by the off-diagonal relaxation terms¹ and can strongly affect absorption in the windows between the lines.² In this paper we deal with a slightly different aspect of the line-coupling problem: When a line is resolved into several components, it may happen that the linewidth parameters are different from those of the original line and also variable within the multiplet. In a previous work³ we measured the PB parameters for the different Stark components of rotational lines of CH_3F and we observed significant variations in the PB coefficients, in agreement with theoretical expectations.

Here we report the first evidence that the hyperfine components of a rotational transition, resolved by nuclear-quadrupole interaction, show significantly different pressure-broadening parameters. We studied the $J = 5 \leftarrow 4$, $K = 4$, $\Delta F = 1$ rotational transition of CH_3I , near 75 GHz, whose wide hyperfine structure allows easy selection of resolved lines. Results are also given for the split Stark components of one of the hyperfine lines and all of the experimental data are explained in terms of a simple theoretical model. Standard theoretical approaches to linewidth computation usually ignored this problem, and previous experiments^{4,5} could not detect the effect; the reason for this is clear within the framework of our theory.

Finally we predict that at higher pressures, when the hyperfine structure would be completely overlapped, line coupling among hyperfine components will affect the PB coefficients. This fact is usually ignored but can be of importance in many studies for which both opposing conditions—resolved or unresolved hyperfine structure—can be met, according to the operating pressure.

II. EXPERIMENT

The experimental apparatus is an evolved version of the setup described in Ref. 3. Only minor improvements

were added for the Stark measurements, while for the measurements on the hyperfine multiplet at null electric field, a different modulation scheme was necessary. The schematic diagram of the latter apparatus is shown in Fig. 1. The hardware for the two approaches is simultaneously present in the experiment, thus allowing cross checks of the results, as described in the following.

The core of the apparatus is a hybrid Fabry-Perot interferometer, enclosed between two conducting plates, to allow the application of a static electric field. The interferometer is filled with the sample gas at room temperature (298–302 K) and the transmission is measured at different pressures (in the range from 1 to 6 Pa) as a function of either the source frequency or the static electric field.

For the case of frequency sweeps at null Stark field, the source is amplitude-modulated at 1 kHz and the signal is processed by a lock-in amplifier. In a preliminary work the center frequencies of the different hyperfine components of interest had been determined with a resolution of a few kHz. The resonator is then carefully tuned to the center frequency of one of the hyperfine components and the computer is programmed to scan the klystron frequency, thus sampling the gas absorption at about 150 data points evenly distributed in a range of 4–5 linewidths across the cavity transmission curve. The scan is repeated without the sample gas and the loga-

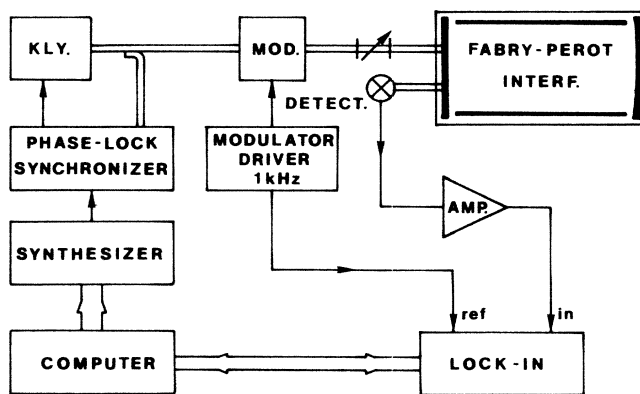


FIG. 1. Schematic diagram of the experimental apparatus used for linewidth measurement at null Stark field.

rithm of the ratio (point to point) is stored as a function of the frequency. Because of the presence of a resonant cavity the line shape so obtained is composed of both an absorption curve and a dispersive component. A composite model line shape⁶ is fitted to the experimental data to determine the Lorentzian half-width at half-maximum (HWHM) at the given gas pressure. Of course we checked the width results against spurious broadening effects by changing the source power and the modulation amplitude; we also tested the importance of frequency detuning between the transition and the cavity center. The sensitivity of the method described here is not as good as that achieved by Stark modulation, but we preferred this method to avoid Stark perturbations of the linewidth.

The rotational spectrum of CH₃I is rather crowded and this severely limits the choice of the components one can study in an accurate and reliable way. We selected the $K=4$, $\Delta F=1$ hyperfine transitions because they are well isolated in the spectrum and also because the theory suggests that the width differences increase with K . We could measure all of them, except the $F=\frac{7}{2} \leftarrow \frac{5}{2}$ transition which partially overlaps with other lines.

The need for well-isolated lines is even stronger for the case of Stark-split components; for this purpose we selected the $F=\frac{5}{2} \leftarrow \frac{3}{2}$ hyperfine line because in weak fields its components do not overlap with other lines within a range of about 40 MHz. We used electric fields always smaller than 180 V/cm, thus the Stark pattern for this line is typically linear, with eight components in symmetrical pairs, labeled by the (F, M) quantum numbers. The procedure for broadening measurements on Stark-split components and the experimental details have been described previously.^{3,7} In short, the klystron and the resonator are tuned to a same off-resonant frequency and the electric field is modulated and swept through resonance. A derivative line shape is recorded and analyzed to provide the width in voltage units; this value is then converted to frequency by a voltage-to-frequency relationship, experimentally calibrated for each component.³

Both the frequency-sweep and the field-sweep experiments provide the linewidth as a function of gas pressure. The pressure-broadening coefficients are determined by fitting a rational expression to the data, in a model⁸ that accurately accounts for Doppler broadening.

As the hyperfine and Stark results are obtained by two substantially different experimental methods, we made a test to verify whether a systematic difference in the re-

sults should be ascribed to the measurement techniques. By means of a constant electric field we selected a single Stark component and we measured its broadening parameter by the frequency-sweep technique. Although less accurate, the result is coincident within experimental error with that obtained by the field-sweep approach.

III. THEORY

The theoretical computation of linewidth parameters for the hyperfine components of the multiplet can be derived from the relaxation matrix of the separate Stark lines. Thus we start with the case of well-resolved quantum numbers M showing that both diagonal and off-diagonal relaxation terms depend on the hyperfine quantum number F . The former contribute to the PB of the Stark resolved lines, the latter only to the zero-field hyperfine lines. It is worth noting that in any case the PB parameters depend on F , but not on the magnitude of the nuclear-quadrupole interaction constant eqQ , provided that it can be neglected in comparison with the rotational energy. As a consequence, our approach is not restricted to cases of large nuclear quadrupole coupling, but it extends to all hyperfine-resolved spectra of symmetric top molecules.

The treatment given in Ref. 3 for the Stark components is now modified in order to deal with the presence of the hyperfine interaction. As in Ref. 3 we assume the weak-field approximation and denote by l_M^ϵ the Stark line

$$|f, J_f, M + \epsilon\rangle \leftarrow |i, J_i, M\rangle.$$

In the present case the labels i and f denote all quantum numbers other than J and M , including F ; M is the z component of F , and ϵ labels the polarization of the radiation field.

In the framework of impact approximation, the relaxation effect on the absorbing molecule of a collision with a perturbing molecule, whose internal state is r , can be described by the operator $P_{MM}^\epsilon(b, v, r)$, defined in the space of the Stark lines. b is the impact parameter and v the relative velocity. The diagonal elements P_{MM}^ϵ contribute to the parameters of the single line l_M^ϵ , while the off-diagonal elements $P_{M\bar{M}}^\epsilon$ describe the coupling between the lines l_M^ϵ and $l_{\bar{M}}^\epsilon$.

$P_{M\bar{M}}^\epsilon$ can be expressed in terms of the collision-scattering matrix $S = 1 - iT$:

$$P_{M\bar{M}}^\epsilon(b, v, r) = \langle [\langle iJ_i, M, rM_r | T(b, v) | iJ_i, \bar{M}, rM_r \rangle + \langle fJ_f, \bar{M} + \epsilon, rM_r | T^+(b, v) | fJ_f, M + \epsilon, rM_r \rangle] \delta_{M\bar{M}} - 2 \sum' \langle iJ_i, M, rM_r | T(b, v) | iJ_i, \bar{M}, r'M_r \rangle \langle fJ_f, \bar{M} + \epsilon, r'M_r | T^+(b, v) | fJ_f, M + \epsilon, rM_r \rangle \rangle_{av}, \quad (1)$$

where \sum' stands for the sum over all primed indices and $\langle \rangle_{av}$ for the average on the states of the perturbing molecule whose magnetic quantum number is M_r . The first two "outer" terms in Eq. (1) are, by symmetry consideration, independent on M and F . As a consequence, the M and F dependence of the PB and the line-coupling effect

are due only to the third "middle" term, bilinear in T .

In order to calculate the scattering matrix we resort, as described in Ref. 3, to the Anderson-Tsao-Curnutte⁹ approach, but different approximations¹⁰ at small-impact parameters can be used as well. Anyhow, for strongly dipolar molecules (such as CH₃I), the choice of one particu-

lar method does not appreciably affect the results of computation. We assume that the interaction between colliding molecules is dominated by dipole-dipole forces and we adopt a perturbative expansion of T at the lowest order in the intermolecular potential. Such a procedure allows us to derive a calculable expression for $P_{MM}^{\epsilon}(b, v, r)$ [Eq. (5) of Ref. 3].

According to the above discussion, the modifications caused by the presence of the hyperfine interactions are restricted to the geometrical factor appearing in the calculation of the middle term. This factor was

$$\langle J_i K | 10J_i K \rangle \langle J_f K | 10J_f K \rangle R_{MM}^{\epsilon} \quad (2)$$

and the same expression holds in the present case, when the necessary modifications to R_{MM}^{ϵ} are introduced. We note that because of the two Clebsh-Gordan coefficients appearing in front of R_{MM}^{ϵ} the middle term is proportional to K^2 . This explains the null experimental results of Refs. 4 and 5 where the line parameters of $J=1 \leftarrow 0$, $K=0$ of CH_3CN and CH_3Cl hyperfine transitions were measured.

The explicit expression for R_{MM}^{ϵ} in the present case is

$$R_{MM}^{\epsilon} = [(2J_i + 1)(2J_f + 1)(2F_i + 1)(2F_f + 1)]^{1/2} (-)^{J_i + F_i + J_f + F_f + 2I} W(J_i J_i F_i F_i; 1I) \\ \times W(J_f J_f F_f F_f; 1I) \langle F_i M | 1M - \bar{M}, F_i \bar{M} \rangle \langle F_f \bar{M} + \epsilon | 1\bar{M} - M, F_f M + \epsilon \rangle, \quad (3)$$

where the W 's are Racah coefficients, and I is the nuclear spin ($I = \frac{5}{2}$ for iodine). We recall that in the absence of hyperfine interaction the right-hand side of Eq. (3) was restricted to the last two Clebsh-Gordan coefficients (with the obvious substitution of J to F).

To compute the width of single-resolved Stark components, the diagonal elements R_{MM}^{ϵ} are of interest; they have the form

$$R_{MM}^{\epsilon} = M(M + \epsilon)G(I, J, F)$$

with

$$G(I, J, F) = \frac{[J_i(J_i + 1) + F_i(F_i + 1) - I(I + 1)][J_f(J_f + 1) + F_f(F_f + 1) - I(I + 1)]}{4[J_i(J_i + 1)J_f(J_f + 1)]^{1/2}[F_i(F_i + 1)F_f(F_f + 1)]}. \quad (4)$$

TABLE I. Calculated and measured self-broadening coefficients (kHz/Pa, HWHM) for the rotational line $J=5 \leftarrow 4$, $K=4$ of CH_3I . Results for both single and simultaneous fits of symmetrical Stark pairs are reported.

Resolved structure	Calculated	Measured	
		Single	Pair
None	63.0		
Hyperfine			
$F = \frac{5}{2} \leftarrow \frac{3}{2}$	78.1	75.5(1.2)	
$F = \frac{7}{2} \leftarrow \frac{5}{2}$	84.2	91.2(1.7)	
$F = \frac{9}{2} \leftarrow \frac{7}{2}$	83.7		
$F = \frac{11}{2} \leftarrow \frac{9}{2}$	80.4	85.8(1.0)	
$F = \frac{13}{2} \leftarrow \frac{11}{2}$	74.8	79.9(1.0)	
$F = \frac{15}{2} \leftarrow \frac{13}{2}$	66.8	66.2(1.0)	
Stark components			
of $F = \frac{5}{2} \leftarrow \frac{3}{2}$			
$M = -\frac{1}{2} \leftarrow -\frac{1}{2}$	111.2	111.9(1.3)	
$M = \frac{1}{2} \leftarrow -\frac{1}{2}$	111.2	111.4(1.4)	111.8(1.3)
$M = \frac{1}{2} \leftarrow \frac{3}{2}$	106.0	105.8(1.3)	
$M = -\frac{1}{2} \leftarrow -\frac{3}{2}$	106.0	105.0(3.4)	105.7(1.3)
$M = \frac{3}{2} \leftarrow -\frac{1}{2}$	106.0	105.2(1.6)	
$M = -\frac{3}{2} \leftarrow -\frac{1}{2}$	106.0	106.8(1.3)	106.5(1.2)
$M = \frac{5}{2} \leftarrow \frac{3}{2}$	88.6	86.9(1.2)	
$M = -\frac{5}{2} \leftarrow -\frac{3}{2}$	88.6	89.9(1.2)	88.3(1.3)

By comparing Eq. (4) with Eq. (7) of Ref. 3 one can conclude that the effects of nuclear quadrupole on the line shape of single Stark components tend to disappear in the limit of $J \gg I$.

From Eq. (3) we can also derive the expression for \bar{R} , which substitutes R_{MM}^{ϵ} in the operator $\bar{P}(b, v, r)$ for the zero-field lines. In fact, in the absence of a Stark field the different components collapse into a single hyperfine line: Then the R_{MM}^{ϵ} factor has to be averaged¹¹ on the line "amplitudes" I_M^{ϵ}

$$I_M^{\epsilon} = [3/(2F_f + 1)]^{1/2} \langle F_i M, 1\epsilon | F_f M + \epsilon \rangle. \quad (5)$$

By use of Eqs. (3) and (5) one obtains

$$\begin{aligned} \bar{R} &= \sum_{M, \bar{M}} I_M^{\epsilon} R_{MM}^{\epsilon} I_{\bar{M}}^{\epsilon} \\ &= \frac{1}{2} [F_i(F_i + 1) + F_f(F_f + 1) - 2] G(I, J, F). \end{aligned} \quad (6)$$

This equation solves the problem of estimating the effect of nuclear quadrupole on the width of each hyperfine line. The results computed by Eq. (6) can be compared with those obtained in the absence of hyperfine interaction.

When $I = 0$ and $J = F$, Eq. (6) gives

$$\bar{R}(I=0) = \frac{J_i(J_i + 1) + J_f(J_f + 1) - 2}{2[J_i(J_i + 1)J_f(J_f + 1)]^{1/2}}. \quad (7)$$

This expression is currently used in the literature even when the hyperfine structure is present and gives the results reported in the first line of Tables I and II. On comparing Eqs. (6) and (7), one can see that this is justified only in the limit $J \gg I$. On the contrary, Eq. (7) holds when the pressure broadening causes the hyperfine structure to collapse into a single unresolved line. This physically would correspond to the case of such a large pressure (usually several kPa) that it completely masks the hyperfine structure.

TABLE II. Calculated and measured self-broadening coefficients (kHz/Pa, HWHM) for the $J=4 \leftarrow 3$, $K=3$ rotational line of $\text{CH}_3^{81}\text{Br}$.

Resolved structure	Calculated	Measured	Ref.
None	88		
Hyperfine			
$F = \frac{5}{2} \leftarrow \frac{5}{2}$	106	99.8(4.5)	13
$F = \frac{7}{2} \leftarrow \frac{7}{2}$	104	99.8(4.5)	13
$F = \frac{9}{2} \leftarrow \frac{7}{2}$	101	99.8(4.5)	13
$F = \frac{5}{2} \leftarrow \frac{3}{2}$	101	95.3	14
Stark components			
of $F = \frac{5}{2} \leftarrow \frac{3}{2}$			
$M = -\frac{1}{2} \leftarrow -\frac{3}{2}$	136	134.6(2.5)	7
$M = \frac{1}{2} \leftarrow -\frac{1}{2}$	143	138.6(2.3)	7

IV. RESULTS AND DISCUSSION

The results of our work are summarized in Table I. It presents the theoretical estimates and it reports all the measured pressure-broadening coefficients, both for the different hyperfine transitions and for the Stark components of the $F = \frac{5}{2} \leftarrow \frac{3}{2}$ hyperfine line. The data for the hyperfine transitions are also displayed in Fig. 2, as an aid in assessing the agreement between theory and experiment about the F dependence of the linewidth parameters.

A few remarks are necessary about the experimental errors quoted in Table I. These experimental errors are essentially statistical and do not include the systematic effects (such as the absolute calibration of the capacitance manometer) which could obscure the relevance of relative values. The accuracy of the Stark technique was discussed in Ref. 3; nonlinearity of Stark effect is particularly troublesome for the $M = (\pm \frac{5}{2}) \leftarrow (\pm \frac{3}{2})$ components and this probably explains the difference in the measured widths of this pair. The hyperfine data are obtained as the small difference between two large signals, so they are intrinsically not very accurate. The composite line shape we used in the analysis describes very well the experimental line shapes, but we did not test the validity of this model in other ways. We estimate that the worst case absolute inaccuracy introduced by the fitting model should be less than 5%, but anyhow it will not affect the relative values for different F 's. For the strongest lines we had to introduce a correction of about 1% caused by the absorption pathlength.

We estimate that the absolute accuracy of theoretical values is about 10%, but the relative accuracy should be far better. A probable explanation of the excellent absolute agreement between theory and experiment must

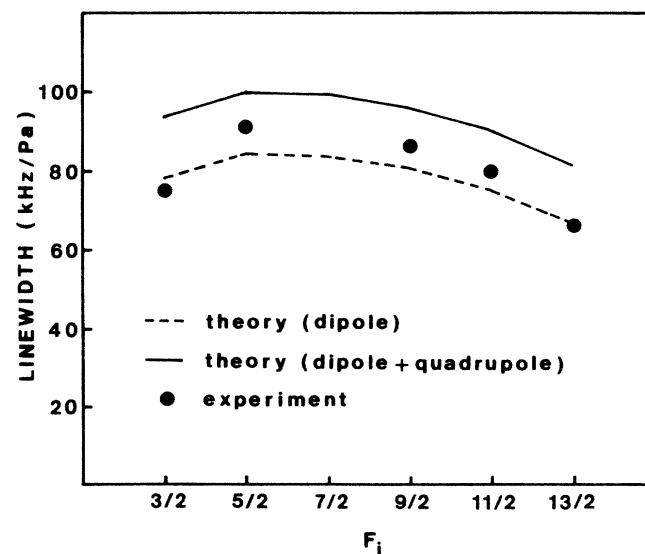


FIG. 2. The linewidth parameter of the $J=5 \leftarrow 4$, $K=4$, $F_i + 1 \leftarrow F_i$ hyperfine transitions of CH_3I is plotted as a function of F_i .

probably be found in the fortuitous balance of two opposite errors. From one hand, Anderson approximation usually produces a small overestimation of the linewidths. On the other hand, we neglected the broadening contribution of interactions other than dipole-dipole. We tried a test computation of the broadening parameters including the dipole-quadrupole and quadrupole-quadrupole interactions, even if the molecular quadrupole Q of CH_3I is not well known. By assuming¹² $Q = 5.35 \text{ D \AA}$ the estimated linewidths are increased of about 15% (see Fig. 2) but the relative trend is nearly unaffected.

A further confirmation of the reliability of our theoretical model comes from comparison with old measurements on CH_3Br obtained in different experiments.^{7,13,14} As shown in Table II, we correctly explain both the increase in the broadening coefficients on resolution of the Stark components and the slight difference in the two measured components; the difference in the hyperfine lines is very small and could not be detected by the exper-

iment of Ref. 13.

In summary, we have obtained experimental evidence of the effect of nuclear quadrupole on the line-shape parameters of rotational lines, and the agreement between theoretical and measured values is particularly satisfactory for three main aspects: (i) The different hyperfine lines show a variable width and the trend with F can be correctly calculated; (ii) the different Stark components of a same hyperfine line show a different broadening and the M dependence is correctly given by the theory; (iii) the line-coupling effects between Stark components cause a zero-field width significantly smaller than the width of each component.

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¹A. Ben Reuven, Phys. Rev. Lett. **14**, 349 (1965); Phys. Rev. **145**, 7 (1966).

²P. W. Rosenkranz, IEEE Trans. Antennas Propag. **AP-23**, 498 (1975); C. Braun, J. Mol. Spectrosc. **93**, 1 (1982); M. O. Bulanin, A. B. Dokuchaev, M. V. Tonkov, and N. N. Filippov, J. Quant. Spectrosc. Radiat. Transfer **31**, 521 (1984); J. Boisssoles, C. Boulet, and D. Robert, Chem. Phys. Lett. **122**, 237 (1985); further contributions can be found in *Spectral Line Shapes*, edited by F. Rostas (de Gruyter, Berlin, 1985), Vol. 3; *Spectral Lines Shapes*, edited by R. J. Exton (Deepak, Hampton, VA, 1987), Vol. 4.

³G. Buffa, A. Di Lieto, P. Minguzzi, O. Tarrini, and M. Tonelli, Phys. Rev. A **34**, 1065 (1986).

⁴R. C. Ham and S. L. Coy, J. Chem. Phys. **74**, 5453 (1981).

⁵G. Buffa, D. Giulietti, M. Lucchesi, M. Martinelli, and O. Tarrini, Nuovo Cimento **7D**, 105 (1986).

⁶A. Dymanus, Physica **25**, 859 (1959).

⁷P. Minguzzi, M. Tonelli, G. Carrara, and A. Di Lieto, J. Mol. Spectrosc. **109**, 395 (1985).

⁸P. Minguzzi and A. Di Lieto, J. Mol. Spectrosc. **109**, 388 (1985).

⁹P. W. Anderson, Phys. Rev. **76**, 647 (1949); C. J. Tsao and B. Curnutte, J. Quant. Spectrosc. Radiat. Transfer **2**, 41 (1962).

¹⁰J. S. Murphy and J. E. Boggs, J. Chem. Phys. **47**, 691 (1968); D. Robert and J. Bonamy, J. Phys. (Paris) **40**, 923 (1979); R. P. Leavitt and D. Korff, J. Chem. Phys. **74**, 2180 (1981).

¹¹G. Buffa and O. Tarrini, Phys. Rev. A **16**, 1612 (1977).

¹²D. L. Vanderhart and W. H. Flygare, Mol. Phys. **18**, 77 (1970).

¹³P. Minguzzi, A. Di Lieto, and M. Tonelli, Ann. Phys. (Paris) **10**, 1065 (1985).

¹⁴J. A. Roberts, T. K. Tung, and C. C. Lin, J. Chem. Phys. **48**, 4046 (1968).