The role of intense line wings in the process of infrared multiple–photon excitation of polyatomic molecules.

V.A.Kuz'menko

Troitsk Institute for Innovation and Fusion Research,
Troitsk, Moscow region, 142190, Russian Federation.

Abstract

The results of experimental testing the existence of intense Lorentzian–like wings with FWHM $\sim 4.5\ cm^{-1}$ in the absorption spectra of polyatomic molecules in a gas phase are presented. Two independent experimental methods were used for evaluating the integral intensity of the line wings for a number of substances. In the first case, the cross–section of the far wings of absorption bands in a gas phase spectrum were measured. Then, these band wings were extrapolated inside the contour of absorption band. In the second case, the saturation degree of the linear spectrum of molecules was determined. Radiation of a pulsed $CO_2$–laser was used at low gas pressure ($\sim 16\ mtorr$) and averaged excitation level of molecules $< n > \sim 0.1\ quanta/molecule$. The values obtained by these two independent methods coincide for a variety of molecules. The average relative integral intensity of the line wings varied from $\sim 0.6\%$ for $SF_6$ and $SiF_4$ to $\sim 90\%$ for $(CF_3)_2O$ and $(CF_3)_2CO$.

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1 Introduction

The phenomenon of the infrared multiple–photon excitation (IR MPE) and collisionless dissociation of polyatomic molecules was discovered in works [1,2]. Numerous works were carried out later aimed to clearify the mechanism of this process. This interest was stimulated by the fact, that the widths both of laser radiation and molecule absorption lines are several orders of magnitude lower, than the anharmonicity of molecular vibrations. In the first work [1] the hypothesis of the existence of the so–called "quasicontinuum" of vibrational states was proposed. Despite some argued criticism [3], this idea has got the broadest distribution.

In the recent years, however, the views on the nature of "quasicontinuum" have changed dramatically. Earlier, it was accepted, that "quasicontinuum" consists of a huge number of narrow lines arising as a result of coupling different vibrational states. Now it is widely believed [4], that the absorption line is unique, but it becomes very wide. The origin of the "quasicontinuum" now is bounded up with intramolecular vibrational relaxation (IVR). This is a reasonable idea. The IVR process can be very fast (picosecond timescale). The corresponding Lorentzian width of the absorption line can be in this case comparable with anharmonicity of the molecular vibrations. The main disadvantage
of this model is that it does not explain how the molecules can be excited in the field of low vibrational levels, where the IVR is absent and the absorption lines remain narrow. Experiments show, that excitation of molecules in this area occurs without essential difficulties, but the theory gives no satisfactory explanation of this fact.

In works [5,6] an idea was proposed, that the IR MPE process is a trivial result of absorption in the area of line wings, but untrivial is the nature of these wings. Practically, the possible role of line wings was not discussed in the literature earlier. It is, apparently, due to the fact, that appropriate estimations can easily be made. The lifetime of excited states of molecules due to spontaneous emission in the infrared region lays in the millisecond timescale. The natural width of line must to be smaller than 100\,Hz. Even for the strongest molecular transitions, at the distance from the line center equal to the value of molecular angarmonicity, the Lorentzian countour of the natural width would have an absorption cross–section smaller then $10^{-25} \, cm^2$. This cross–section cannot play any appreciable role in overcoming the angarmonicity of molecular vibrations.

However, such an estimation has not been tested in experiment earlier. It is possible to assume, that for some unknown reasons, intensity of real line wings is much higher, than the theory predicts. How high the intensity of line wings should be to explain the observable effect of laser excitation of molecules? Rather correctly such information can be derived from the experimental results of works [7-9], where the depletion of rotational states of \textit{SF}_6 molecules by TEA CO$_2$–laser radiation was studied in the conditions of molecular jet. The results of such processing are presented in Fig.1. Except for the usual narrow component of the line with a Doppler width $\sim 30\, MHz$, the wings, or more precisely speaking, a wide component of the line should exist with a cross–section $\sigma \simeq 6 \cdot 10^{-20} \, cm^2$ and with a Lorentzian full width at half medium $2\Gamma \simeq 4.5 \, cm^{-1}$. The relative integral intensity of this component is rather small, $X \sim 0.2\%$, but it is high enough for efficient excitation of molecules from all rotational states.

The purpose of the present work is an experimental testing the hypothesis of the existence of intense line wings. First of all, it is important to point out that the Lorentzian countor is rather flat and the wings of the line can manifest themselves as far natural wings of absorption bands. Numerous literature exists about the far wings of absorption bands for small and light molecules which are due to collisional broadening of the lines [10,11], but publications devoted to the far wings of absorption bands in the gas phase for heavy polyatomic molecules are absent. In the present work, for the first time, far natural wings of absorption bands are discovered for a number of polyatomic molecules. The experiments show, that the absorption cross–section in the region of these far band wings is independent on the gas pressure. Measuring the intensity of the far band wings allows to estimate the relative integral intensity of the line wings.

On the other hand, it is important to pay attention to the phenomenon of saturation of the absorption spectrum of polyatomic molecules by laser radiation at low gas pressure [12]. It is well known, that for some molecules this saturation can be very pronounced, but for the others it is minimal [13]. A satisfactory
explanation of this distinction was not found. From the point of view of the discussed hypothesis, the distinction is due to the difference in relative intensities of the line wings: for the molecules with a large relative intensity of the line wings the saturation is minimal and vise versa.

So, the saturation degree of the absorption spectrum of polyatomic molecules can be used to estimate the relative integral intensity of the line wings. With this purpose, in the presented work, the saturation degree of the linear absorption spectra of a number of molecules by the TEA $CO_2$–laser radiation was investigated. The measurements were conducted in comparable conditions at low gas pressure and at average level of molecular excitation $< n > \sim 0.1$ quanta/molecule. It was supposed, that under these conditions the narrow component of the line is completely saturated, but the wide one is not. Then the measured saturation degree can be regarded as a rough estimation of the relative integral intensity of the line wings. Estimations of the line wings intensity obtained by two independent methods were compared with each other for a number of molecules.

2 Experimental

The TEA $CO_2$–laser with an additional low pressure cell inside the resonator was used. When a low pressure cell was switched on, the TEA $CO_2$–laser switched from the multimode regime to the single–mode one. Using a nitrogen free gas mixture allowed to obtain a pulse of generation with $\sim 150 ns$ duration at half height without a "tail".

A piroelectric detector was used for measuring the laser radiation absorption at low gas pressure. The technique of experiments is similar to that described in [14]. The piroelectric detector was placed inside the cell (pass length 110 cm) on the distance 10 mm from the laser beam. Calibration of the detector’s sensitivity was carried out by measuring the attenuation of the transmitted beam at relatively high gas pressure ($> 100 mTorr$).

Measurements of the absorption cross–section in the region of the far band wings in some cases were carried out with an optico–acoustic detector (OAD). This detector was also used to study the influence of the buffer gas pressure on the intensity of the far band wings. In the last case, first of all, the dependence of the OAD sensitivity on the gas pressure was measured. The cell was filled with $\sim 40 mTorr$ of hexafluoroacetone and it was irradiated by TEA $CO_2$ laser on 10R(12) line with energy $\sim 1mj$. Under these conditions, the amount of energy, absorbed in the cell, remains constant, and the dependence of the OAD signal on the buffer gas (nitrogen) pressure, becomes the dependence of the detector’s sensitivity on the gas pressure. Then the cell was filled with 1 Torr of the substance to study ($CF_2Cl_2$, $SiF_4$) and 1 – 800 Torr of nitrogen was added. The energy of a pulse laser radiation was usually 30 – 70 mj and it’s wavelength was selected in the region, where the far band wings had sufficiently clean countor and the absorption cross–section in the range $10^{-21} – 10^{-22} cm^2$.

An IR–spectrophotometer with a stainless steel cell (pathlength 10 cm and
gas pressure up to 5 atm) was used to study the absorption band profile for a number of molecules. Most of the used substances were commercially available and had been used without purification. Completely fluoreneted dimethyl ether was obtained by rectification of the products’ mixture after fluorenation of the dimethylether. The gas used in the experiments contained ~ 97% of the basic substance. As an impurity, (~ 3%) of the CF₃H was present.

3 Results

Typical results of the experimental study are presented in Figs. 2 and 3. These pictures show the saturation degree of linear absorption spectrum by pulse laser radiation of the SF₆ and (CF₃)₂CO molecules. In the first case the saturation is very high, and in the second one it is minimal in full agreement with early results [13,15]. At average level of excitation ~ 0.1 quanta/molecule, with 1 atm of buffer gas added, the measured absorption cross-section of the laser radiation practically coincides with the same cross-section (σ₀), obtained with a spectrophotometer.

Table 1 contains main results of these experiments.

Table 1. Determination of the saturation degree of the linear absorption spectrum of polyatomic molecules by pulse CO₂–laser radiation.

| N  | Molecule   | Laser line | Fluence mJ/cm² | Pressure mTorr | σₘ/σ₁ | < n >* | σ₁/σ₀ % |
|----|------------|------------|----------------|----------------|-------|--------|----------|
| 1  | SF₆        | 10P(20)    | 32             | 16             | 2.0   | 0.15   | 0.6      |
|    |            |            | 32             | 100            | 1.8   | 0.25   | 1.0      |
| 2  | SiF₄        | 9P(34)     | 32             | 100            | 1.4   | 0.07   | 1.0      |
| 3  | CF₃Cl₂      | 10P(36)    | 32             | 100            | 1.3   | 0.06   | 1.5      |
| 4  | CF₃Cl₃      | 9R(30)     | 32             | 100            | 1.4   | 0.07   | 4.0      |
| 5  | C₂F₃Cl    | 9R(6)      | 32             | 100            | 1.4   | 0.15   | 12       |
|    |            |            | 32             | 100            | 1.3   | 0.35   | 7.0      |
|    |            |            | 3.2            | 100            | 1.3   | 0.55   | 11       |
|    |            |            | 3.2            | 100            | 1.4   | 0.09   | 17.5     |
| 6  | CH₃SiF₃   | 10R(26)    | 32             | 16             | 1.05  | 1.0    | 80       |
|    |            |            | 32             | 100            | 1.05  | 0.1    | 90       |
| 7  | (CF₃)₂O    | 10R(20)    | 32             | 16             | 1.00  | 1.00   | 2.8      |
|    |            |            | 3.2            | 100            | 1.00  | 1.00   | 70       |
| 8  | (CF₃)₂CO   | 10R(14)    | 32             | 16             | 1.00  | 1.00   | 3.0      |
|    |            |            | 3.2            | 100            | 1.00  | 1.00   | 3.0      |
| 9  | C₆H₅SiF₃  | 10R(10)    | 32             | 16             | 1.00  | 3.0    | ≥ 90     |

* < n > = σ₁F/hν

The measured absorption cross-sections are usually greater for multimode laser radiation (σₘ) than for the singlemode one (σ₁) [16]. Owing to limited
sensitivity of the piroelectric detector the minimum used gas pressure was chosen 100 mTorr in some cases. For these cases, the obtained final value \( X = \sigma_1 / \sigma_0 \) is overestimated by a factor of \( \sim 1.6 \).

In Fig.4, the spectral dependence of the absorption cross-section of \( SiF_4 \) molecules around the \( \nu_3 \) absorption bands is presented. The edges of the absorption band have approximately an exponential form, the slope being greater for the blue side, than for the red one. At the distance more than \( 25-40 \text{ cm}^{-1} \) from the band center, much more sharply sloping wings are observed. The curve (2) is a Lorentzian profile with FWHM \( 2\Gamma = 4.5\text{cm}^{-1} \), which passes through the point with minimal absorption cross-section in the given spectral range. So, we can see, that far band wings have a Lorentzian behavior.

In Fig.5 a spectral dependence of the absorption cross-section of \( SF_6 \) molecules is shown. In this rather typical case the far band wings are masked by intense combination bands.

The same results for the \( CF_2Cl_2 \) molecules are shown in Fig. 6. In the latter case the far band wings can be observed in rather limited spectral range \( 950 - 1000\text{cm}^{-1} \).

Fig.7 shows the spectrum of the \( (CF_3)_2O \) molecules. The basis of the spectral dependence well coordinate with a Lorentzian contour, which center coincides with the most intense absorption band. It can be seen also, that intensity of the Lorentzian contour in this case approximately two orders of magnitude higher, than for the cases of \( SiF_4 \) and \( SF_6 \) molecules, although the intensities of the strongest absorption bands are comparable for all these molecules.

The experiments have shown, that the absorption cross-section of the investigated molecules in the region of far wings of their absorption bands depends neither on it’s own gas pressure, nor on the buffer gas pressure (in the range 8– 800 Torr of nitrogen). It means, that the far wings of absorption bands are natural and have no relation to the collisional broadening of the lines.

The computed relative integral intensities of the line wings are listed in Table 2. It was supposed, that \( 2\Gamma = 4.5\text{cm}^{-1} \) in all cases. For comparison, the final results of Table 1 are also shown here. It is visible, that the difference in relative integral intensities of the line wings reaches two orders of magnitude for different molecules. At the same time, the maximum deviation between the estimations, obtained by two independent methods, does not exceed three times. The intensity of the line wings is rather small for the molecules with one central atom and grows quickly with increasing the number of atoms and branching degree of the molecules.
Table 2. Evaluation of the relative integral intensity of the line wings.

| N | Molecule       | X % | From the band wings | From the saturation degree |
|---|----------------|-----|---------------------|----------------------------|
| 1 | SiF₄            | 0.6 | 0.6                 |                            |
| 2 | SF₆             | 0.8 | 0.6                 |                            |
| 3 | CF₂Cl₂          | 1.6 | 0.9                 |                            |
| 4 | CFCI₃           | 2.3 | 2.5                 |                            |
| 5 | C₂F₃Cl          | 3.0 | 7.5                 |                            |
| 6 | CH₃SiF₃         | 11  | 11                  |                            |
| 7 | (CF₃)₂O         | 36  | 90                  |                            |
| 8 | (CF₃)₂CO        | 40  | 90                  |                            |
| 9 | C₆H₅SiF₃       | 50  | ≥ 90                |                            |

4 Discussion

Close, although not so precise as from works [7-9], estimations of the parameters of the wide component of line for SF₆ molecules (σ ≈ 10⁻¹⁹ cm² and Γ < 3 cm⁻¹) can be obtained by processing the experimental results of work [17]. In this latter work the absorption of CW CO₂-laser radiation by SF₆ molecules was studied in the molecular beam conditions, and the autors dealt practically only with the line wings.

A substantial difference exists between the estimations of the relative integral intensity of the line wings for SF₆ molecules, derived from works [7-9] (X ≈ 0.2%) and obtained in the present work (X = 0.6 – 0.8%). This is obviously due to the fact, that in the first case the molecules were located at a zero vibrational level, and the second estimation is obtained for the room temperature, when the majority of molecules is in different excited states. The strong temperature dependence of the laser radiation absorption by SF₆ molecules [17] allows to assume, that the intensity of line wings substantially grows with increasing the level of vibrational excitation of molecules. This is maybe the main physical reason of formation of ensembles of "hot" and "cold" molecules under action of the pulse CO₂ laser radiation [18].

It is visible from Table 2, that for the largest molecules a systematic underestimation exists when the intensity of the far band wings is used. This is maybe due to the real width of line wings for large molecules is smaller, than it was supposed in calculations. Such an assumption agrees with the results of experimental study of photodissociation of a number of molecular dimers in [19], where the the autors dealt generally with the same wings of lines. With increasing the molecular weight the spectral photodissociation width of the corresponding dimer usually decreases: for (C₂H₄)₂, (SiF₄)₂, and (SF₆)₂ the corresponding values are 12, 4.7, and 1.5 cm⁻¹, accordingly.

The difference in absorption of the singlemode and multimode laser radiation has, obviously, common nature with a similar effect, observed earlier in works [16,17]. This is possible only in the conditions, when the IVR process is absent in
a molecule. Therefore, it can be expected, that in the \((CF_3)_2CO\) and \(C_6H_5SiF_3\) molecules the fast IVR occurs already after the absorption of the first quantum of \(CO_2\) laser radiation. More precisely this question could be clarified after studying the full spectrum of these molecules in the conditions of a free jet, when the IVR process can frequently be identified [20].

The results of the present work, combined with experimental data of works [7-9, 17], provide quite sufficient proof of existence of the intense line wings in polyatomic molecules. The nature of these wings can be related with breaking the mechanism of averaging the molecular inertia moment on the timescale of vibrational motion. The spectroscopic methods allow a high precision determination of the inertia moment of a molecule, this moment being an averaged inertia moment because it changes by \(5-10\%\) on the timescale of vibrational motion [21]. If one supposes that the mechanism of averaging the inertia moment can suffer periodic short–time breakings (destructions) by various vibrational modes, then we should get a clump of lines in the spectrum instead of a single narrow line. The width of this clump of lines must apparently be determined by the maximum amplitude of the molecule inertia moment variations due to vibrations. Such the objects have been intensively studied in the last years, and the authors tried to explain their nature by coupling of different vibrational modes [22]. The very moment of breaking-up (destruction) can be considered as some short–life ”stressed” state of the molecule, which should be corresponded with some wide component in the line spectrum. So, while it is not clear, which effect is responsible for the spectral width of such a component, it is worth noting, that the width itself, retrieved from the experiments, is comparable to the period of vibrational motion of atoms in a molecule.

Molecular beam with a cryogenic bolometer is ideally suitable for the study of line wings. Narrow and powerful laser radiation interacts mainly with the line wings [17]. Low rotational temperature in the beam results in that the width of the absorption band is comparable with or less than that of the line wings. Therefore, for precise determination of the width of the line wings it is not necessary to investigate very far wings of the absorption bands. The sensitivity of the apparatus can easily be calibrated using large polyatomic molecules like hexafluoroacetone. Upon calibration, such an instrument can be used for measuring the intensity and the width of the line wings for most polyatomic molecules. Using one \(CO_2\)–laser, we can measure the line wing parameters for the \(1 \leftrightarrow 0\) transition. Having two \(CO_2\)–lasers, we can obtain the same information for the \(2 \leftrightarrow 1\) transition and even for the \(3 \leftrightarrow 2\) one ( if at the first step we make use of one of the twoquantum transitions, studied in [23] ).

## 5 Conclusion

The discussed experimental results quite clearly show the existence of intense line wings of unknown nature in polyatomic molecules. This line wings are interesting in itself. But it is also very important, that such kind of experiments [17] gives for the present day the only straightforward experimental proof of the
strong time invariance violation in a photon-molecule interaction [24,25].
So, the task of experimental study of the line wings of polyatomic molecules
has a great importance. Unfortunately, the experimentalists are afraid to work
with this interesting and unusual physical object.

References

[1] N.R.Isenor, V.Merchant, R.S.Hallsworth and M.S.Richardson Can.J.Phys. 51,1281(1973).
[2] R.V.Ambartzumian, V.S.Letokhov, E.A.Ryabov and N.V.Chekalin JETPh Lett 20,597(1974).
[3] V.T.Platonenko JETPh Lett. 25,52(1977).
[4] V.S.Letokhov, E.A.Ryabov, A.A.Makarov et. al. "Laser Spectroscopy of
Vibrationally-Excited Molecules". Moscow, Nauka (1990).
[5] V.Yu.Baranov, A.P.Dyad’kin and V.A.Kuz’menko Kvantov.Elektron. 15,732(1988).
[6] V.A.Kuz’menko Preprint of the Institute of Atomic Energy 4886/12, Moscow (1989).
[7] V.M.Apatin, V.M.Krivtsun, Yu.A.Kuritsyn, G.N.Makarov and I.Pak
Opt.Commun. 47,251(1983).
[8] Yu.A.Kuritsyn, G.N.Makarov, I.Pak and M.V.Sotnikov JETPh 94,65(1988).
[9] I.Pak Dissertation, Moscow (1989).
[10] L.I.Nesmelova, C.D.Tvorogov and B.B.Fomin "Spectroscopy of Line
Wings" Novosibirsk,(1977). (in Russian)
[11] M.V.Tonkov, N.N.Filippov, Yu.M.Timofeyev and A.V.Polyakov
J.Quant.Spectr.Rad.Transf. 56,783(1996).
[12] O.P.Judd J.Chem.Phys. 71,4515(1979).
[13] W.Fuss and K.L.Kompa Progr.Quant.Electr.7,117(1981).
[14] R.V.Ambartzumian, G.N.Makarov and A.A.Puretzky Opt.Commun. 34,81(1980).
[15] W.Fuss, K.L.Kompa and F.M.G.Tablas Faraday Discuss. 67,180(1979).
[16] J.L.Lyman and K.M.Leary J.Chem.Phys. 69,1858(1978).
[17] C.Liedenbaum, S.Stolte and J.Reuss Chem.Phys. 122,443(1988).
Fig. 1 Profile of absorption line of $SF_6$ molecules for the $\nu_3$ band 1 $\leftarrow$ 0 transition.

Fig. 2 Spectral dependence of the absorption cross-section of multimode laser radiation by $SF_6$ molecules. $32 $mj/cm$^2$. 
$-16$ Torr $SF_6$. 
$0 -16$ Torr $SF_6 + 760 $Torr $N_2$. 
Linear room temperature absorption spectrum of $SF_6$ molecules is also shown.

Fig. 3 Spectral dependence of the absorption cross-section of multimode laser radiation by $(CF_3)_2CO$ molecules. $32 $mj/cm$^2$. 
$-16$ Torr $(CF_3)_2CO$. 
$0 -100$ Torr $(CF_3)_2CO + 760 $Torr $N_2$. 
The solid curve represent a linear room temperature absorption spectrum of $(CF_3)_2CO$ molecules.

Fig. 4 Spectral dependence of the room temperature absorption cross-section of $SiF_4$ molecules.
1- spectrophotometer result. 
2- Lorentzian profile with FWHM $= 4.5$ cm$^{-1}$.

Fig. 5 Spectral dependence of the room temperature absorption cross–section of $SF_6$ molecules.
1- spectrophotometer result. 
2- Lorentzian profile with FWHM $= 4.5$ cm$^{-1}$.

Fig. 6 Spectral dependence of the room temperature absorption cross–section of $CF_2Cl_2$ molecules.
1- spectrophotometer result. 
2- Lorentzian profile with FWHM $= 4.5$ cm$^{-1}$.

Fig. 7 Spectral dependence of the room temperature absorption cross–section of $(CF_3)_2O$ molecules.
1- spectrophotometer result. 
2- Lorentzian profile with FWHM $= 4.5$ cm$^{-1}$. 

[18] V.N.Bagratashvili, V.C.Doljikov and V.S.Letokhov JETPh 76,18(1979). 
[19] R.E.Miller J.Phys.Chem. 90,3301(1986). 
[20] E.R.Th.Kertsel, K.K.Lehmann, T.F.Mentel, B.H.Pate and G.Scoles J.Phys.Chem. 95,8282(1991). 
[21] S.J.Cyvin ”Molecular Vibrations and Mean Square Amplitudes”. Oslo(1968). 
[22] K.K.Lehmann, G.Scoles and B.H.Pate Ann.Rev.Phys.Chem. 45,241(1994). 
[23] A.Linskens, S.L.Hekkert and J.Reuss Infrared Phys. 32,259(1991). 
[24] V.A.Kuz’menko, E-print hep-ph/0002084 
[25] V.A.Kuz’menko, E-print physics/0102038
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Fig. 3 Spectral dependence of the absorption cross-section of multimode laser radiation by (CF$_3$)$_2$CO molecules.
Fig. 4 Spectral dependence of the room temperature absorption cross-section of SiF$_4$ molecules.
Fig. 5 Spectral dependence of the room temperature absorption cross-section of $\text{SF}_6$ molecules.
Fig. 6 Spectral dependence of the room temperature absorption cross-section of $\text{CF}_2\text{Cl}_2$ molecules.
Fig. 7 Spectral dependence of the room temperature absorption cross-section of $(\text{CF}_3)_2\text{O}$ molecules.