

IS “DARK WATER” REALLY DARK?

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We consider features of experimental studies performed by microwave spectroscopy methods and showing the collisional pressure broadening of molecular lines by hydrogen at very low temperatures. It is shown that the effect of preferential adsorption of orthohydrogen by the walls of the gas cell of a spectrometer can influence significantly the measurement results and lead to an erroneous interpretation of the data given by astrophysical studies of the interstellar space.

1. INTRODUCTION

Recently, the capabilities and significance of microwave spectroscopy methods in astrophysics have increased greatly. As earlier, they are mainly applied in the millimeter and submillimeter bands of electromagnetic waves, where the spectral lines determined by molecules have the highest intensity. At present, promising research instruments are brought out of the Earth's atmosphere which is absorbing in those bands. An instrument that is typical of modern astrophysical microwave spectroscopy is a superheterodyne high-resolution spectrometer HIFI mounted onboard the HERSCHEL spacecraft. Thousands of spectral lines of the molecules in the interstellar space turn out to be observable by means of the HIFI spectrometer and are intensely studied within the framework of the international project “HIFI Consortium,” which includes about 30 research institutes and universities in Europe, USA, and Canada.

Interpretation of the observed spectra requires laboratory studies of the parameters of the spectral lines present. The methods of measuring the frequencies of the lines of motionless molecules, which have been developed well by now, as well as interpretation of broadband molecular spectra is beyond the scope of this work. We focus on laboratory measurements of collisional parameters of spectral lines under conditions that are close to those of the interstellar medium, wherever possible. The most important parameter is the low temperature in the range from about 10 to 100 K, which is typical of molecular space clouds. The radiation of interstellar molecules is sustained by their continuous excitation due to collisions, primarily with hydrogen molecules which are most widespread in the interstellar medium. The hydrogen molecule itself is nonpolar, and its spectrum is not observed in the microwave range. During such collisions, the kinetic energy of the hydrogen molecules transforms to the rotational energy of other, mainly polar molecules which then radiate it in the form of spontaneous emission observed by radio telescopes.

The notion “dark water” was introduced in [1, 2] and reflects the essence of the experimental results of studying the collisional broadening of spectral lines of water molecules due to their collisions with hydrogen molecules, which is considered in detail below. They show that at low temperatures, contrary to the theoretical predictions, the broadening coefficient starts decreasing sharply. This means that the efficiency of collisional excitation of the corresponding energy states in water molecules should also decrease sharply with decreasing temperature. Along with this, the intensities of the corresponding spectral lines, which are recorded by a radio telescope, will decrease, as well. Thus, even if there are many water molecules in

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the interstellar medium, their rotational lines should have a low intensity. Therefore, unlike the conditions typical of, e.g., the Earth's atmosphere, the water molecules in the interstellar clouds radiate weakly, i.e., they are "dark."

The unexpected results of [1, 2] and the new imposing notion became widespread fastly. The hypothesis proposed in [3] allowed one to explain the experimental dependencies observed in [1] without revision of the existing theories of intermolecular interaction. Nevertheless, the authors of [1, 2] in their reply [4] doubt that hypothesis. Moreover, in works [5–11], which were published later than [3], the results of [1] that corresponded to the "dark water" concept were regarded as at least one of the possibilities. In some works, these results were adopted unconditionally, while in other works, as possible variants. Some works regarded them as possible evidence for new collisional dynamics in collisions of the H_2 and H_2O molecules. This situation required detailed analysis of the experimental conditions along with the data obtained by low-temperature measurements of the collisional line broadening [1, 12–15] as well as the corresponding theoretical calculations [7] and the hypothesis proposed in [3]. Such an analysis is the purpose of this paper.

2. COLLISIONAL EXCITATION AND LINE BROADENING

The mechanism of collisional excitation underlies the processes of cooling of interstellar gas clouds. Spontaneous emission of the collision-excited molecules leads to a decrease in their energy and, eventually, to gas cooling and is determined by the well-known Einstein coefficient A . In its turn, the excitation efficiency depends on the cross section of collisions of the studied molecules with the hydrogen molecules which are most widespread in space. The collision cross section can be determined from quantum-mechanical calculations or measured experimentally. At present, there are well-developed methods of calculating the parameters of the molecules, which are of interest to us. However, it is always necessary to compare the results of calculations with the experiment, which allows one to determine their quality and accuracy limits. In the laboratory, one usually measures the broadening of spectral lines of the studied molecules due to their collisions with the molecules or atoms of the required gas, which is recalculated to find the collision cross section. This method has been used with considerable success for sufficiently high temperatures that are typical of the Earth's atmosphere (see, e.g., [16]). However, the extension of these methods to the low-temperature region is hindered by the condensation of virtually all gases that are of interest for astrophysics, which happens during this process. In space, this process is strongly decelerated by the absence of walls, whereas in the laboratory, the sizes of the spectrometer cells are small, and the condensation occurs almost instantaneously. To circumvent this problem, the so-called collisional-cooling method was developed [17]. It uses the dynamic regime of observation of the spectral lines: the gas, the broadening of the spectral lines of which is studied, is released continuously through a heated pipe into the cold spectrometer cell filled with a certain amount of the "buffer" gas, i.e., the gas that does not condense yet at the temperature of the experiment (usually, it is helium or hydrogen) and is used as the collision partner. Without the "buffer" gas, which fills the cell, the studied gas would have condensed on the cell walls immediately. However, in the cell with the "buffer" gas, the condensation process is slowed down due to the diffusion of the studied gas through the "buffer" one. As a result, the studied gas which enters the cell freezes on the walls continuously, but the time of diffusion of its molecules from the source towards the wall is sufficient to measure the broadening of the studied line by the "buffer" gas at the temperatures below the condensation temperature of the studied gas. Such experiments were first performed with helium, and were extended later to hydrogen. These two gases form an exhaustive list of the "buffer" gases used in this method, but they play a significant role in space.

3. STUDIES OF COLLISIONAL BROADENING IN THE LOW-TEMPERATURE REGION

In the first experiments, an application of the collisional-cooling method with helium as the buffer gas [17, 18], it was noted that the experimental and calculated values of the collisional-broadening parameters agree within the measurement error. Unexpected facts were observed when the hydrogen-broadened lines of the H_2O and CO molecules were studied in a wide temperature range [13, 15].

It should be noted that the qualitative behavior of the temperature dependence of line broadening due to collisions is determined by the usual thermodynamic properties of gases. When a gas cools down, the number of molecules per unit volume in it increases in inverse proportion to the temperature. In this case, the average thermal velocity of the molecules decreases in direct proportion to the square root of the temperature. The average time between the collisions is inversely proportional to the result of the simultaneous action of these two mechanisms and, therefore, varies in direct proportion to the square root of the temperature. The collisional broadening is inversely proportional to the average time between the collisions, i.e., it is inversely proportional to the square root of the temperature. Strictly speaking, this power-law dependence of the collisional broadening on the temperature is accurate only for a perfect gas. The theoretical calculations which allow for particular energy states of molecules and the features of intermolecular interactions during collisions make it possible to refine the power-law index, but do not change the qualitative behavior.

Instead of a monotonic increase in the line broadening with decreasing temperature, which is predicted from theoretical considerations, the experiments in [13, 15] revealed two different regions. Namely, at higher temperatures, the behavior of the line broadening due to the collisions with hydrogen molecules agreed well with the expected one, but in the case of cooling below 40 K for the line $J'_{Ka'Kc'} \leftarrow J_{KaKc} = 1_{10} \leftarrow 1_{01}$ of the H_2O molecule [13] and below 28 K for the line $J = 5 \leftarrow 4$ of the CO molecule [14], the broadening decreased sharply as the temperature decreased, which did not agree with the well-known theoretical results. For the line $J = 5 \leftarrow 4$ of the CO molecule, the broadening started to increase again at the temperatures below 20 K. These measurements, which were in principle isolated, had no significant consequences, and the found disagreement with the theory was regarded, on the one hand, as an indication of the necessity of a more rigorous quantum calculation in the low-temperature region and, on the other hand, as an indication of the necessity of more extensive and accurate experimental studies.

A much more significant study of six lines of water, which belonged to the terahertz frequency range, was performed by the same group at the Jet Propulsion Laboratory assigned by NASA to support the studies of the HERSCHEL space observatory and other space research instruments, such as SWAS, “Odin,” etc., with laboratory data [1]. Both the American and the European space agencies attach great importance to studies of water in space. For example, a key HERSCHEL program with the guaranteed observation time is the WISH program [14] accomplished jointly by researchers from many countries. First of all, it is necessary to study the cross sections of collisions of the H_2O molecule with its main collision partner, i.e., the H_2 molecule, which is required to convert the observed line intensities to the number density of molecules in space (see, e.g., [19]). With no allowance for the cost of production and maintenance of a spectrometer and development of the measurement techniques, the effort of the JPL group spent on these studies can be estimated by calculating the net observation time, which is equivalent to 360 days of continuous operation of properly functioning equipment for an 8-hour working day. These studies of collisions of water and hydrogen molecules at low temperatures are pioneering and unique so far. Therefore, it is no surprise that both the studies themselves and the processing of their results have received much attention.

The main result obtained in [1] was the reproducibility of a sharp decrease in the broadening with decreasing temperature already for six spectral lines of water, which cannot be explained by the existing theories. The authors of [1] fitted the experimental dependencies together with the empirical curves which did not correspond to any physical model, did not explain this sharp decrease, but assessed the astrophysical consequences of the observed phenomenon. In the materials of the paper itself and the presentation at the largest international spectroscopy conference of 2010 in Columbus (USA), which was called “Dark water” [2], two factors were indicated as such consequences: first, elimination of water as the main cooler of cold interstellar gas clouds, which slows down their collapse, i.e., the star formation process, and, second, the necessity to revise the existing estimates of the amount of water molecules in gas clouds and make it much greater. Both factors were related to a sharp decrease in the cross section of the water–hydrogen collisions at low temperatures, i.e., with a sharp weakening of the collisional excitation of water molecules by hydrogen molecules. It was also stated that the unobserved “dark” water can be the storage of bound oxygen.

The authors of [1] studied the broadening of the lines $1_{11} \leftarrow 0_{00}$, $2_{02} \leftarrow 1_{11}$, $1_{10} \leftarrow 1_{01}$, $3_{12} \leftarrow 2_{21}$,

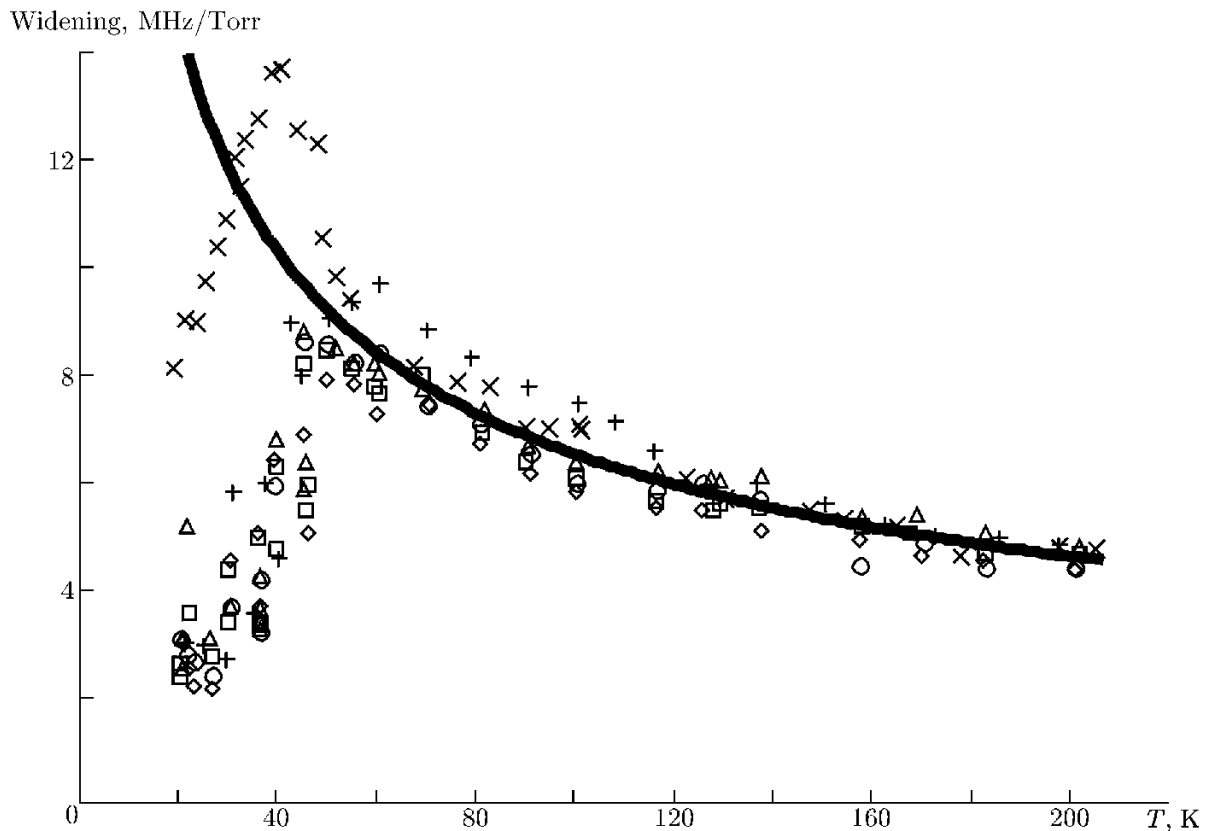


Fig. 1. Experimentally measured values of the broadening parameter of six lines of water [1] as functions of the temperature T for the lines $1_{11} \leftarrow 0_{00}$ (Δ), $1_{10} \leftarrow 1_{01}$ (\times), $2_{02} \leftarrow 1_{11}$ (+), $3_{12} \leftarrow 2_{21}$ (\circ), $3_{12} \leftarrow 3_{03}$ (\square), and $3_{21} \leftarrow 3_{12}$ (\diamond). The bold curve shows the usual power-law dependence of the broadening with the power-law index $x = -0.5$.

$3_{12} \leftarrow 3_{03}$, and $3_{21} \leftarrow 3_{12}$ of the water molecule H_2^{16}O . The experiment was performed using the collisional-cooling method in the temperature range from about 20 to 200 K, and the pressure range 0.1 to 1.5 Torr of hydrogen acting as a “buffer” gas. In [1], the temperature of the gas in the cell was determined from the Doppler width of the line under small pressures. In addition, it should be noted that the temperature of the cell walls, which was measured by a thermometer, turned out to be 30–40 K lower than the gas temperature, which will be discussed later. The combined results of those measurements are presented in Fig. 1. The plot demonstrates similar behavior of the broadening for all water lines under consideration, and only the line $1_{10} \leftarrow 1_{01}$, which was measured separately from other lines, shows slight qualitative deviations that are, evidently, related to somewhat different experimental conditions. This similarity is observed despite the fact that the frequencies of the studied lines differ by more than twice, namely, from 0.556 to 1.16 GHz, the rotational quantum numbers J take the values from 0 to 3, and the lower-level energies, from 0 to 173 cm^{-1} . The bold line in Fig. 1 also shows the extrapolation of the temperature dependence of the broadening from the high-temperature region to the low-temperature region. It corresponds to the usual power-law dependence with the power-law index $x = -0.5$.

4. FEATURES OF HYDROGEN MOLECULES AS COLLISION PARTNERS OF WATER MOLECULES

As is known (see, e.g., [20]), there can be two spin modifications of the H_2 molecule, namely, the orthostate in which the total spin of the nuclei is equal to unity, and the parastate in which the total spin of the nuclei is equal to zero. It follows from the symmetry of wave functions that orthohydrogen can be only

in the states which are odd with respect to the rotational quantum number J , while parahydrogen, only in the even states. Due to the light weight of the H_2 molecule, the distances between its rotational levels exceed their average thermal energy even at room temperature. The ratio of the number of the H_2 molecules in the orthostates to that in the parastates is equal to 3, i.e., the statistic ratio of the number densities of the ortho- and parahydrogen (the ortho/para ratio) is equal to 3. Although this value corresponds to the high-temperature limit, it is approximately valid at room temperature and corresponds to the so-called “normal” hydrogen. As the temperature decreases, the ortho/para ratio under conditions of the equilibrium of the ortho- and parastates decreases (see the equations in [20]). At a low temperature, only the lowest rotational levels turn out to be populated, which correspond to parahydrogen with $J = 0$ and orthohydrogen with $J = 1$. Even at 80 K, the summation with respect to all other levels changes the ortho/para ratio by less than 1%. Therefore, in the low-temperature regions, either the “para” and “ortho” notations, or $J = 0$ and $J=1$, are frequently used. The transitions between the ortho- and parastates are prohibited, and the process of hydrogen conversion between the ortho- and parastates is slow at low temperatures. Allowance for the composition of gaseous hydrogen in terms of the spin states is important for spectroscopy because of a significant difference between the H_2 molecules in the $J = 1$ (ortho) and $J = 2$ (para) states, namely, the anisotropy and isotropy of the interaction potential, respectively, or, using a more conventional “spectroscopic language,” the presence or absence of the quadrupole momentum of the molecule. This basic difference determines different cross sections of their collisions with other molecules, which are certainly greater for orthohydrogen. This effect was revealed experimentally rather long ago in collisions with ammonia [21]. The difference obtained theoretically for the collisions of the H_2 molecules with the H_2O molecules amounts to about an order of magnitude at low temperatures [22, 23]. The same difference leads to different features of the interaction with surfaces, which will be considered in the next section.

5. PREFERENTIAL ADSORPTION

Orthohydrogen is adsorbed on various adsorbers stronger than parahydrogen. This phenomenon, which was called preferential adsorption, was discovered at a temperature of 90 K for the adsorption on TiO_2 [24]. Later, it was observed on many other adsorbers, e.g., $\gamma - \text{Al}_2\text{O}_3$ [25], Alcoa activated alumina, which consisted mainly of Al_2O_3 and AlOOH [26], and on carbon nanotubes [27] at different temperatures from 12 to 90 K. The preferential adsorption can manifest itself very strongly. For example, it served as the basis for creation of a pilot device capable of producing up to 40 l of metastable orthohydrogen with a purity of 99% a day under standard conditions, namely, at a temperature of 273 K and a pressure of 760 Torr [25]. Recall that in [1], where the hydrogen pressure varied from 0.1 to 1.5 Torr, the adsorbed amount of hydrogen is negligible compared with that capacity. The coefficient of hydrogen separation with respect to the spin states due to the preferential adsorption increases with decreasing temperature. According to measurements, it is equal to 1.6 at 90 K [24], and 16 [28] or even 39 [26] at 20.4 K.

One of the best adsorbers is the so-called amorphous water ice [29]. It is formed when water molecules freeze slowly from the vapor phase on a sufficiently cold surface. Under these conditions, the condensing molecules are insufficiently mobile to form a crystal line structure, and the formed condensed mass has a significant internal energy since it is amorphous, microporous, and characterized by a huge adsorbing surface [30]. The adsorption capacity of amorphous ice is characterized by that the area of its efficient adsorbing surface per mass can reach a value ranging from 400 m^2/g [1] to several thousands of square meters per gram [32], which is comparable with the adsorptivity of absorbent carbon. For the case of adsorption on amorphous ice, the anisotropic part of interaction of orthohydrogen with the surface can be represented as an electrostatic interaction of the partial charges on the surface molecules with the quadrupole momentum of the H_2 molecule [29].

The phenomenon of preferential adsorption has not been given much attention in the microwave spectroscopy. Apparently, this is due to the fact that it required a “fateful coincidence” to manifest itself, which occurred in the experiments with the collisional cooling of water [1] where hydrogen was used as the

buffer gas, the molecules of which were partly subject to preferential adsorption, and the best of adsorbers (amorphous ice) was formed inevitably and continuously on the walls of the spectrometer cell.

6. WHAT HAPPENS IN THE COLLISIONAL-COOLING CELL?

The authors of [1] did not allow for the possibility of variations in the spin composition of hydrogen in the cell and believed, as the authors of [12], that the hydrogen in the cell retained the same ortho/para ratio equal to 3, as in the initial cylinder. It is indicated above that this would be valid if one allowed for only the conversion between the spin states, which, being a slow process, could not change the gas composition during the experiment. However, adsorption is a fast process. As it has already been mentioned, the wall temperature measured in [1] with a thermometer was significantly lower than the gas kinetic temperature measured from the Doppler line broadening. This difference was reflected, in particular, in the fact that in Fig. 2 of [1] and in Fig. 1 of this work, a sharp decrease in the broadening parameter of the $1_{11} \leftarrow 0_{00}$ line occurs at about 45 K, whereas in Fig. 2 of [7], where the same experimental data (which one can see from the references and the spread of points) are analyzed in comparison with the theoretical calculations, a sharp decrease occurs at about 80 K. Evidently, the horizontal axis in [1] corresponds to the temperature of the sensor on the cell wall, while in [7], to the gas temperature. Thus, the strong decrease in the broadening observed in [1] started at gas temperatures of 70–80 K, which corresponded to the sensor temperature 32–43 K on the cell wall, and continued, when the temperature dropped by another 20–30 K, i.e., to the wall temperature about 10 K. In this case, the latter turned out to be sufficiently low to ensure a sufficiently high coefficient of separation with respect to the spin states in the measurement range. It was shown in [33] that the amorphous ice, or, more exactly, such its kind as high-density amorphous ice, which is the best adsorber, is easily formed at $T < 40$ K on any surface with a high thermal conductivity (in particular, on the surface of aluminum, of which the collisional-cooling cell was made in the experiments described in [1] and which was mentioned in earlier paper [15] by the same authors. For the water, which is a polyamorphous substance, the temperature 30–40 K is the beginning of the region of the phase transition between the high-density amorphous ice forming at lower temperatures and the low-density amorphous ice forming at higher temperatures [33]. The preferential adsorption of orthohydrogen on amorphous ice in the case where normal hydrogen having the ortho/para ratio equal to 3 was released into the vacuum chamber with amorphous ice was specially studied and calculated in [29]. At 12 K, the infrared spectrum of orthohydrogen only was observed in the spectrum of the newly formed adsorber layer, and the authors estimated the content of parahydrogen in the layer as $5 \pm 5\%$, which agrees with the value calculated by them, i.e., approximately 7%. Thus, all the conditions for the formation of amorphous ice on the cell wall were fulfilled precisely in the experiment [1].

7. *AB INITIO* CALCULATIONS AND INTERPRETATION OF EXPERIMENTAL DATA

To explain the unusual dependencies obtained in [1], the authors of [7] performed the most accurate (up to now) *ab initio* calculation of the broadening of two of the six lines of water, which were studied in [1]. The authors of [7] obtained good agreement in the high-temperature region (Fig. 2) and strong mismatch of the calculated and experimental results in the low-temperature region, and provided two possible explanations to this fact: (i) inapplicability of the “shock approximation” and (ii) “dramatic conversion of hydrogen between spin states” (the terms will be explained below).

Note that the shock approximation was used in [1] indirectly to determine the collisional width of the line by fitting its analytical form obtained within the framework of the shock approximation to match the observed profile. Using a profile that did not correspond to the experimental conditions would certainly yield a systematic error in the determination of the broadening parameter. However, there is no mentioning in [1] about any changes in the line shape under various experimental conditions. From the viewpoint of calculations, the inapplicability of the shock approximation corresponds to the necessity of allowing for “collisional resonances” or formation of short-lived complexes. However, the influence of the “resonances”

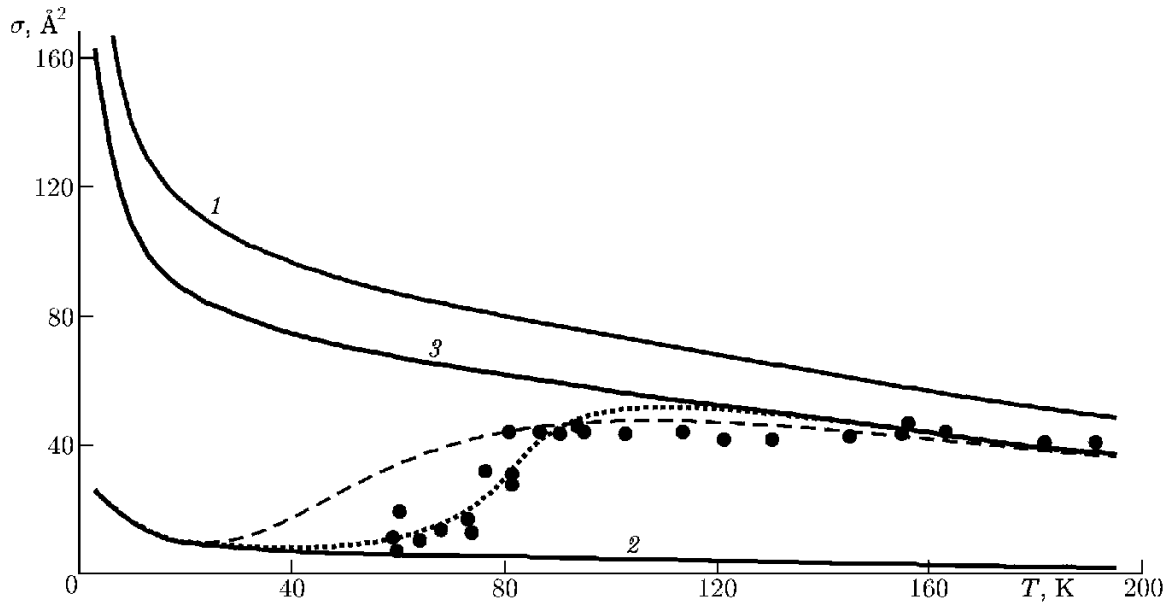


Fig. 2. Cross section σ of the collisional interaction for the line $1_{11} \leftarrow 0_{00}$ of the H_2O molecule. The dots show the experimental values [1] based on the data of [7] (see the text). Curves 1, 2, and 3 illustrate the calculations performed in [7] for orthohydrogen, parahydrogen, and “normal” hydrogen with the ortho/para ratio equal to 3, respectively. The dashed curve corresponds to the equilibrium value of the ortho/para ratio for each temperature. The dotted curve shows the qualitative dependence corresponding to a change in the spin composition of hydrogen due to the preferential adsorption.

is not seen on the theoretical curves of the temperature dependence on the collision cross sections in [7]. It was revealed that the conclusion on the inapplicability of the shock approximation was based rather on a misunderstanding, but it is still worth paying attention, because the erroneous results turned out to be quick-spreading. As an example, we can mention paper [5], in which this explanation is assumed to be proven with reference to [7], although the authors of [7] did not perform any calculations or estimations that would demonstrate any improvement in the agreement of the theory and the experiment in the case of allowance for the inapplicability of the shock approximation.

Consider the conditions of applicability of the shock approximation by following paper [34] also referred to by the authors of [7]. It is necessary to do this, since Eq. (5) in [7] contains an evident misprint. The shock approximation means that the time of the collisional interaction of molecules is much shorter than the time between collisions. It is applicable in the case of fulfillment of the condition given in [34] that the interaction volume, or the collision volume U is small compared with the volume per molecule in gas: $U \ll n^{-1}$, where n is the number density of molecules. The quantity U is defined as

$$U = v\sigma\tau/2,$$

where v is the mean velocity, σ is the collision cross section of molecules, and τ is the collision time, which is defined in [7] as

$$\tau = 1/(2\pi\Gamma),$$

where Γ is the width of the collisional resonance, i.e., the characteristic peaks which arise, as demonstrated by the *ab initio* calculations, on the plot of the collision cross section as a function of the interaction energy and correspond to the resonant collisional interaction of molecules in certain states under certain conditions in a cooled gas (see, e.g., [35]).

Let us estimate the condition of applicability of the shock approximation, using the values of the parameters used in [7], namely, $T \sim 80$ K, $\sigma \sim 50$ Å² (which corresponds to $5 \cdot 10^{-15}$ cm²), $v \sim 1$ km/s and

the resonance linewidth $\Gamma \sim 1 \text{ cm}^{-1}$ (which corresponds to $3 \cdot 10^{10} \text{ Hz}$,¹) and the experimental conditions [1], namely, the pressures 0.1–1.5 Torr (which corresponds to 13.3–200 Pa). The interaction volume calculated from these data is equal to $1.3 \cdot 10^{-21} \text{ cm}^3$. For unknown reason, the authors of [7] believed that the number density n of molecules in the experiment in [1] was equal to about 10^{20} cm^{-3} , referring to a private communication of B. Drouin. As a result, they concluded that the shock approximation is inapplicable, using the equality of the volume per molecule $n^{-1} \sim 10^{-20} \text{ cm}^3$ and the estimated interaction volume 10^{-20} cm^3 .

The number density of molecules can be estimated from the law of the perfect gas state as

$$n = L \frac{273}{T} \frac{p}{760},$$

where $L = 2.69 \cdot 10^{19}$ is the Loschmidt number, i.e., the number density of molecules for $T = 273 \text{ K}$ and the pressure $p = 760 \text{ Torr}$, which corresponds to 101 kPa. Under the experimental conditions of [1], $n \sim 1.21 \cdot 10^{16} \text{ cm}^{-3}$ for a pressure of 0.1 Torr, and $n \sim 1.82 \cdot 10^{17} \text{ cm}^{-3}$ for a pressure of 1.5 Torr, which corresponds to the volume per molecule $8.26 \cdot 10^{-17} \text{ cm}^3$ for a pressure of 0.1 Torr, and $5.49 \cdot 10^{-18} \text{ cm}^3$ for a pressure of 1.5 Torr. Thus, in the entire pressure range used in the experiment in [1], the volume per molecule correspondingly turns to be greater than the interaction space by 4000 to 60000 times and, hence, the condition of applicability of the shock approximation is fulfilled with a sufficient margin. As a result, the inapplicability of the shock approximation cannot serve as an explanation of the great mismatch of the experimental and theoretical results in [7].

The second explanation of this difference is the possible role of the hydrogen conversion between the spin states: “It is also possible that due to the reasons that are still unknown, a dramatic conversion of molecules of orthohydrogen to molecules of parahydrogen at low temperatures occurs, which is determined by some paramagnetic impurities in the cell walls, although so far there are no experimental hints at this explanation” [7].

By the “dramatic conversion,” the authors of [7] mean the hypothetical phenomenon, which would decrease the ortho/para ratio in the spectrometer cell from the “normal” value at the spectrometer input down to the value corresponding to the thermodynamically equilibrium Boltzmann distribution for each temperature within a time that is shorter than the time of the experiment, which is equal to about 16 min for the measurement of the line profile at one point [1].

Consider the results shown in Fig. 1 and 2 of [7], and in Fig. 2 of this paper, where one can see the calculated dependencies of the cross sections of interaction between the H_2O molecules and the molecules of ortho- and parahydrogen [7], as well as the points showing the experimental results of [1]. The calculated curves demonstrate the expected difference between them, which is about one order of magnitude in accordance with [22, 23], and an increase in both cross sections with decreasing temperature. The same figure shows the line corresponding to the calculated collision cross section determined by the “normal” hydrogen with the ortho/para ratio equal to 3, which was expected in the experiment [1]. Recall that this value of the ortho/para ratio characterizes the hydrogen only at the device input. The figures also show the dashed curves which correspond to the ortho/para ratio which is equilibrium at each point, i.e., the result of the “dramatic conversion” mentioned in [7]. Herein, paper [20] was used to plot this curve. One sees that there

¹ It should be noted that the way in which the authors of [7] determined the interaction time from the linewidth $\Gamma \sim 1 \text{ cm}^{-1}$ of the collisional resonance, is rather questionable. This width is obtained in the calculations of the interaction between the H_2O molecules and parahydrogen for significantly lower temperatures [35]. The greater part of the broadening is determined by the molecules of orthohydrogen, which should primarily be allowed for when considering the interactions. It was noted in paper [36], which dealt with the calculations of the interaction between water and orthohydrogen, that in this case, the resonances do not play a significant role after averaging over the interaction energies, in contrast to the case of interaction with the molecules of parahydrogen [35]. Moreover, one can see in Fig. 8 of [12] that even before averaging, the resonances are almost invisible on the curve of the energy dependence of the cross section of collisions between the molecules of orthohydrogen and CO at temperatures exceeding 30 K, and do not change the shape of the curve even at lower temperatures. It means that the actual interaction time is much shorter than that obtained for $\Gamma \sim 1 \text{ cm}^{-1}$ in accordance with the given formula. Moreover, there are no peaks of collisional resonances on the calculated curves in [7].

are entire regions of low temperatures, namely, $T < 70$ K in Fig. 1 of [7], $T < 80$ K in Fig. 2 of [7], and Fig. 2 of this work, where the experimental values of the collision cross sections, which reflect the corresponding ortho/para ratios, become smaller than the values calculated for the thermodynamic equilibrium in gas. There exist experimental points located up to 4.5 times lower than the curve corresponding to the equilibrium values of the ortho/para ratio, which cannot be explained by the conversion process. The conversion can only decrease the ortho/para ratio from the “normal” value, i.e., 3, down to the corresponding equilibrium value which corresponds to this temperature.

Thus, the “dramatic conversion” considered in [7] cannot explain the strong difference between the experimental and theoretical data not only because its physical mechanism is not clear, but also because it does not describe the experimental results [1].

In real situations, the existence of a whole region of low temperatures, where the experimental value of the ortho/para ratio becomes smaller than its value determined from the condition of the thermodynamic equilibrium in a gas, indicates that a different, non-conversion mechanism causes variations in the populations of the levels of ortho- and parahydrogen, for which the thermodynamic equilibrium in a gas is not the limit. This mechanism is known and consists in the above-mentioned preferential adsorption of orthohydrogen on the cell walls (see, e.g., [24–27, 29]). The action of this mechanism explains a decrease in the ortho/para ratio to the values which are lower than those determined by the thermodynamic equilibrium in gas at a given low temperature.

Under the conditions of a limited amount of hydrogen in the cell [13], the preferential adsorption of the orthohydrogen molecules on the cell walls leads to the enrichment of a gas sample in the molecules of parahydrogen, for which the cross section of collisions with water molecules is an order of magnitude smaller than that for the molecules of orthohydrogen and, consequently, to a decrease in the line broadening parameter of water, which was observed in the experiment [1]. Certainly, the variation of the ortho/para hydrogen ratio influenced the broadening of all the observed lines of the H_2O molecule in the same way. This was the explanation given in [3].

8. DISCUSSION

Qualitatively, the behavior of the broadening and the collision cross section, which is linearly related to the broadening, can be described in the case of a decreasing temperature with allowance for the preferential adsorption of orthohydrogen as (i) the initial motion along the curve of the temperature dependence for normal hydrogen, for which the values of these parameters increase, (ii) then the transition from the curve for normal hydrogen to the curve for parahydrogen, which corresponds to a decrease in the values of these parameters, and, (iii) finally, another increase in their values with the further temperature decrease, but already along the parahydrogen curve. In Fig. 2, this process is shown by a dotted curve, which was plotted using the exponential “switching” function with empirically chosen parameters. Both branches of this dependence can be seen only in [15] for the line broadening of the CO molecule due to the collisions with the H_2 molecules. In considered work [1], where the lines of the H_2O molecules broadened due to the collisions with the hydrogen molecules, the temperature region which corresponded to the second increase in the values of the above-mentioned parameters was not studied.

Note one significant difference between the experiment with the collisional cooling and “usual” experiments studying the adsorption, in which a specially prepared surface was used singly (see, e.g., [32]). In the experiment with the collisional cooling, which is considered here, the adsorber surface was constantly renewed by releasing the vapors of H_2O into the spectrometer cell continuously. The experiment in [37] demonstrates that porous amorphous water, which has frozen over even non-porous water ice in an amount of 10^{15} molecules per 1 cm^2 that corresponds to one monomolecular layer, changes the ice adsorption properties with respect to hydrogen by adding “new places” with enhanced adsorption energy and making the adsorption energy distribution almost indiscernible from that for monolithic porous amorphous ice. Using good linearity of the pressure dependence of the collisional width of the studied lines, which was demonstrated in [1], one can evidently state that in the experiments with the collisional cooling, the layer of the

amorphous ice formed on the walls corresponded at each temperature value to exactly this temperature in terms of the ice kind, adsorption properties, and the coefficient of spin state separation, and was “fresh,” i.e., had the highest adsorption capacity according to [33] and contained vacant positions with all possible adsorption energies [32]. Recall that for amorphous substances, phase transition regions rather than phase transition points exist, and the properties of amorphous ice depend also on the method of its production [32, 33].

The consequences of the ambiguity introduced by the presence of the significantly different values of the cross sections of the $\text{H}_2\text{O}-\text{H}_2$ collisions in the experimental study [1] and theoretical calculations [22, 23] manifested themselves in work [9], which described the processing and interpretation of the data of the HERSCHEL space observatory. Since the authors of [9] had no information on which of the values of the collision cross section should be preferred, they used both values and obtained, correspondingly, two results when calculating the profile of the $1_{10}-1_{01}$ line for one of the observed space source. These results had opposite signs and drastically differed in form (see Fig. 3 in [9]).

The mechanism of changes in the sample composition, which was considered comprehensively in this work, evidently influenced the results of [12] and [13], where the method of collisional cooling was used to study the broadening of the lines $J = 1 \leftarrow 0$, $J = 2 \leftarrow 1$ and $J = 5 \leftarrow 4$ of the CO molecule in the microwave spectral region due to the collisions with the H_2 molecules at low temperatures. In Fig. 10 of [12], both the experimental and calculated dependencies of the collision cross sections are given for the $J = 1 \leftarrow 0$ line. At the temperatures below 25 K, the calculated cross sections for orthohydrogen turn out to be higher by 30% than those for parahydrogen. The data about the adsorption of the H_2 molecules on ice from the CO molecules are almost absent. It is known that there exists the amorphous form of ice of the CO molecules (see, e.g., [38] and references therein), but the corresponding data are rather sparse. However, it is known that the energy of adsorption of the H_2 molecules on the ice of the CO molecules is a factor of about 2.5 lower than the energy of adsorption of the H_2 molecules on ice of the H_2O molecules [39]. This agrees with a significantly smaller difference between the collision cross sections for ortho- and parahydrogen in the case of collisions with the CO molecule for a decreasing temperature [12] compared with the difference between the cross sections for ortho- and parahydrogen in the case of collisions with the H_2O molecule [7, 22, 23], where it amounts to approximately one order of magnitude. In [12], for the temperature region $T > 100$ K, where the usual spectroscopy methods were used, the experimental points lie between the calculated curves for para- and orthohydrogen with accuracy up to the experimental errors, i.e., they are located where the curve for the “normal” hydrogen (with the ortho/para ratio equal to 3) would lie, which demonstrates that the experiment and the calculations agree in this temperature region. In the range of temperatures $T < 25$ K, where the collisional-cooling method was used, the experimental points lie almost precisely, with accuracy up to the experimental errors, on the curve calculated for parahydrogen. This would show the agreement of the calculation and the experiment, if one assumed that the same adsorption mechanism of enrichment of the gas inside the cell in parahydrogen molecules works for the molecular pair H_2-CO and for the pair $\text{H}_2-\text{H}_2\text{O}$ considered here. Being convinced that the composition of hydrogen in the cell coincides with the “normal” composition of the hydrogen in the cylinder, i.e., is characterized by the ortho/para ratio equal to 3, the authors of [12] attributed a mismatch of about 30% between the experimental data and the curve calculated for normal hydrogen (see Fig. 10 in [12]) to the calculation inaccuracy, which was estimated by them as about 30% in the low-temperature region. Similar dependencies can be seen on other plots in [12]. It follows from the results of our work that the experiment and calculation in [12] agree with accuracy exceeding 30% by several times, and the results of [12] are indicative of the fact that the mechanism of the preferential adsorption of orthohydrogen on the cell walls also acts in this case. This conclusion is confirmed by considering the results of the independent experiment presented in [15] and studying the broadening of the $J = 5-4$ line of the CO molecule due to the collisions with the H_2 molecules and He atoms. In that work, in the low-temperature region, i.e., at temperatures about 20–30 K, the above-described behavior change in the broadening parameter was observed (it is seen in Fig. 8 of [15]) that as the temperature decreased, the broadening first increased, then decreased, which corresponded to

the enrichment of the sample in the parahydrogen molecules, and then increased again, but already along the parahydrogen curve. Unfortunately, that work does not present the calculation of the cross section of collisions with the H_2O molecules for the molecules of ortho- and parahydrogen separately, as in [12]. As a rough guide, one can indicate the calculated curve for helium in Fig. 8 of [15]. It is known that the properties of helium, with respect to collisions, are much closer to parahydrogen than to orthohydrogen (see, e.g., [12]). It should be taken into account that the temperatures indicated in [15] were measured on the cell walls, and a spectrometer with the collisional cooling was the same as that used later in [1]. This allows one to assume that there are differences between the temperatures of the gas and the walls, similarly to the differences found in [1].

The phenomenon of the preferential adsorption of the orthohydrogen molecules is in fact universal, since it is caused by basic physical differences in the kinds of the H_2 molecule. The formation of amorphous kinds of ice including metastable ones, is also a rather common phenomenon since it is related to the fact that at sufficiently low temperatures, the molecules condensed on a surface from rarefied vapors have insufficient energies to be transformed to stable crystalline ice which has minimum energy (see, e.g., [30, 40]).

9. CONCLUSIONS

1. Unusual dependencies of the broadening of spectral lines of water due to collisions with the H_2 molecules at low temperatures [1] do not reflect a new physical phenomenon. They are caused by variations in the number density of hydrogen in the ortho- and para-states, which are due to the preferential adsorption of the orthohydrogen molecules on the cell walls covered with amorphous ice under the conditions of the collisional-cooling experiments, and by the fact that the cross section of collisions of the H_2O molecules with the parahydrogen molecules that predominantly remain in the gas is an order of magnitude smaller. This conclusion confirms both the hypothesis advanced in [3] and the validity of the theoretical calculations in [7], and makes the term “dark water” redundant since it has no actual physical meaning in this context.

2. To interpret the data of astrophysical observations and the corresponding calculations, one should use the temperature dependencies of the collision cross sections, which are calculated *ab initio* until new experimental data appear, which allow for the preferential adsorption of the orthohydrogen molecules.

3. The results of the works studying the cross sections of collisions in the molecular pair $\text{H}_2\text{--CO}$ at low temperatures [12, 15] require partial revision since the above-considered mechanism is rather general, and its allowance improves the agreement between the calculation and the experiment by several times.

4. The phenomenon of the preferential adsorption of the orthohydrogen molecules should be allowed for when performing low-temperature spectroscopic experiments with hydrogen as the “buffer” gas.

5. To eliminate the main source of errors when using hydrogen in the experiments with the collisional cooling, separate studies of the collisional interaction of the analyzed gas with pure ortho- or hydrogen, which can be now done experimentally, is the best available way. ²

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REFERENCES

1. M. J. Dick, B. J. Drouin, and J. C. Pearson, *Phys. Rev. A*, **81**, 022706 (2010).
2. B. J. Drouin, M. J. Dick, J. C. Pearson, and E. A. Bergin, in: *65th Int. Symp. on Molecular Spectroscopy, Columbus, Ohio, USA, 2010*, p. 88. http://molspect.chemistry.ohio-state.edu/symposium_65.
3. A. F. Krupnov, *Phys. Rev. A*, **82**, 036703 (2010).
4. B. J. Drouin, J. C. Pearson, and M. J. Dick, *Phys. Rev. A*, **82**, Art. no. 036704 (2010).

² While the paper was considered by the Editors, the authors of [1] made a conference presentation [41] to demonstrate the experimental results which confirmed the validity of the conclusions made herein.

5. E. F. Van Dishoeck, L. E. Kristensen, A. O. Benz, et al., *Publ. Astron. Soc. Pacific*, **123**, 138 (2011)..
6. E. Van Dishoeck, in: *COST Conf., Grenoble, France, 2010*.
http://www.strw.leidenuniv.nl/WISH/wish_results.php.
7. L. Wiesenfeld, and A. Faure, *Phys. Rev. A*, **82**, 040702(R) (2010).
8. E. A. Bergin, M. R. Hogerheijde, C. Brinch, et al., *Astron. Astrophys.*, **521**, L33 (2010).
9. P. Caselli, E. Keto, L. Pagani, et al., *Astron. Astrophys.*, **521**, L29 (2010).
10. Ad van der Avoird and D. J. Nesbitt, *J. Chem. Phys.*, **134**, 044314 (2011).
11. B. J. Drouin, in: *The 21st Int. Conf. on High Resolution Molecular Spectroscopy, Poznan, Poland, 2010*, p. 215.
12. M. Mengel, D. C. Flatin, and F. C. De Lucia, *J. Chem. Phys.*, **112**, 4069 (2000).
13. M. J. Dick, B. J. Drouin, and J. C. Pearson, *J. Quant. Spectrosc. Radiat. Transfer*, **110**, 619 (2009).
14. <http://www.strw.leidenuniv.nl/WISH/>.
15. M. J. Dick, B. J. Drouin, T. J. Crawford, and J. C. Pearson, *J. Quantum Spectrosc. Radiat. Transfer*, **110**, 628 (2009).
16. M. Yu. Tretyakov, G. Yu. Golubyatnikov, V. V. Parshin, et al., *Radiophys. Quantum Electron.*, **51**, No. 9, 713 (2008).
17. J. K. Messer and F. C. De Lucia, *Phys. Rev. Lett.*, **53**, 2555 (1984).
18. D. R. Wiley, D. Bittner, and F. C. De Lucia, *Mol. Phys.*, **67**, 455 (1989).
19. E. F. Van Dishoeck, *Europhys. News*, **42**, 26 (2011).
20. L. Farkas, *Ergebn. Exakt. Naturwiss.*, **12**, 163 (1933).
21. T. Oka, in: B. H. Andrew, ed., *Interstellar Molecules*, Reidel, Dordrecht (1980), p. 221.
22. T. R. Phillips, S. Maluendes, and S. Green, *Astrophys. J. Suppl. Ser.*, **107**, 467 (1996).
23. M.-L. Dubernet, F. Daniel, A. Grosjean, et al., *Astron. Astrophys.*, **460**, 323 (2006).
24. Y. L. Sandler, *J. Phys. Chem.*, **58**, 58 (1954).
25. M. J. Clouter, *J. Phys. E*, **5**, 1099 (1972).
26. I. F. Silvera, *Phys. Rev. Lett.*, **37**, 1275 (1976).
27. R. A. Trasca, M. Kostov, and M. W. Cole, *Phys. Rev. B*, **67**, Art. no. 035410 (2003).
28. C. M. Cunningham and H. L. Johnston, *J. Am. Chem. Soc.*, **80**, 2377 (1958).
29. V. Buch and J. P. Devlin, *J. Chem. Phys.*, **98**, 4195 (1993).
30. V. Buch, *J. Chem. Phys.*, **96**, 3814 (1992).
31. E. Mayer and R. Pletzer, *Nature*, **319**, 298 (1986).
32. L. Amiaud, J.-H. Fillion, S. Baouche, et al., *J. Chem. Phys.*, **124**, 094702 (2006).
33. P. Jenniskens, D. F. Blake, M. A. Wilson, and A. Pohorille, *Astrophys. J.*, **455**, 389 (1995).
34. M. Baranger, *Phys. Rev.*, **111**, 481 (1958).
35. M.-L. Dubernet and A. Grosjean, *Astron. Astrophys.*, **390**, 793 (2002).
36. A. Grosjean, M.-L. Dubernet, and C. Ceccarelli, *Astron. Astrophys.*, **408**, 1197 (2003).
37. J.-H. Fillion, L. Amiaud, E. Congiu, et al., *Phys. Chem. Chem. Phys.*, **11**, 4396 (2009).
38. E. Dartois and S. Baurecker, *J. Chem. Phys.*, **128**, 154715 (2008).

39. T. J. Lee, *Nature Phys. Sci.*, **237**, 99 (1972).
40. J. C. Brandt, in: L.-A. McFadden, P. R. Weissman, and T. V. Johnson, eds., *Encyclopedia of the Solar System*, Elsevier, Amsterdam (2007), p. 557.
41. B. J. Drouin, J. C. Pearson, L. Wiesenfeld, and A. Faurem, in: *66th Int. Symposium on Molecular Spectroscopy, Columbus, Ohio, USA, 2011*, p. 155.
http://molspect.chemistry.ohio-state.edu/symposium_66/symposium/Program/TF.html.