# Collision-induced line-shape effects limiting the accuracy in Doppler-limited spectroscopy of $H_2$

P. Wcisło,[1,2,*] I. E. Gordon,[1] C.-F. Cheng,[3] S.-M. Hu,[3] and R. Ciuryło[2]
[1]*Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA*
[2]*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*
[3]*Hefei National Laboratory for Physical Sciences at Microscale, iChEM, University of Science and Technology of China, Hefei, 230026 China*
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Recent advances in theoretical calculations of $H_2$ dissociation energies and ultra-accurate measurements of $H_2$ transition frequencies give possibilities not only for testing QED and relativistic effects, but also for searching for physics beyond the standard model. In this paper we show that at the level of $10^{-4}$ cm$^{-1}$ the uncertainty of the Doppler-limited $H_2$ line position determination is dominated by collisional line-shape effects. We question the paradigm that the unperturbed transition energy can be determined from linear extrapolation of the line shift to zero pressure.

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## I. INTRODUCTION

Recent developments in the calculation of dissociation energies of molecular hydrogen and its isotopologs [1–4] open a way for testing relativistic and quantum electrodynamics theories as well as for searching new exotic physics, such as additional long-range hadron-hadron interactions [5,6], which goes beyond the standard model. Such tests require very accurate experimental determination of the energies of the molecular hydrogen transitions. Two different experimental strategies have been applied for this purpose. The first one uses Doppler-free spectroscopy of rovibronic transitions, which are characterized by a narrow linewidth [7–11] (of the order of 40 MHz). The second approach takes advantage of the Doppler-limited measurements of electric quadrupole rovibrational transitions [12–21], for which the consequences of a relatively large linewidth (of the order of 1 GHz) are compensated with a high signal-to-noise ratio (SNR) [22–25]. It was demonstrated for a $CO_2$ transition that the Doppler-limited spectroscopy allows the molecular line positions to be determined with accuracy approaching the kHz level, which corresponds to $10^{-7}$ cm$^{-1}$ [26]. However, the intensities of molecular hydrogen quadrupole lines are exceptionally low. It makes the experimental studies of these transitions very challenging. At present, cavity ring-down spectroscopy assisted by an optical-frequency comb [13,26–29] seems to be the most appropriate approach for such studies. It takes advantage of cavity-enhanced sensitivity [15,30–32] and the absolute-frequency scale provided by the optical frequency comb [33–36]. Even using those techniques such a high SNR cannot be achieved at very low pressures. Moreover, the sensitivity of the hydrogen rovibrational transitions to the new hypothetical forces beyond the standard model [5,6] is expected to increase with the difference of the vibrational quantum number in the upper and lower states, which further dramatically decreases the intensities of the targeted transitions. Hence, for this purpose the very high SNR measurements are limited to relatively high pressures only, well beyond the collision-free regime.

In this paper we show that the strong speed dependence of the line shift, which is characteristic for molecular hydrogen, results in asymmetry [37–39] of the Doppler-limited profile. We demonstrate that it leads to nonlinear behavior of the frequency at maximum absorption as a function of pressure. This behavior is determined not by the line-shift speed dependence only, but also by more refined effects originating from the competition between the shift speed dependence and the velocity-changing collisions [19,39,40]. For the Doppler-limited measurements, aiming at the line position determination accuracy at the level of $10^{-4}$ cm$^{-1}$ and lower, the collisions that are improperly taken into account can be the main source of systematic errors. Its importance for the comparison between the experimental line positions and *ab initio* prediction was first demonstrated, for the case of $H_2$ Raman transitions, in pioneering work by Sinclair *et al.* [41].

In Sec. II, as a reference, we perform a simple analysis of the random noise in the Doppler-limited spectroscopy. We determine an optimal choice of the pressures at which the spectra should be collected. This allows the statistical uncertainty of the zero-pressure transition frequency to be averaged down most efficiently. In Sec. III we extend this discussion by the systematic errors caused by the improper inclusion of collisions in the line-shape analysis. It is shown, for the case of the $H_2$ $Q(1)$ (1-0) line, how the systematic error scales with the choice of the pressure range. We demonstrate that the nonlinear behavior of the position of the line maximum with pressure limits the applicability of the simple idea of linear extrapolation of the line shift to zero pressure. Finally, in Sec. IV we reanalyze the experimental spectra from Ref. [17]. We show that the uncertainty budget from Ref. [17] should be completed with the predominant contribution of the systematic error originating from the improper inclusion of collisions in the data analysis.

## II. STATISTICAL UNCERTAINTY

In this section we assume that the measurements of the line position $\omega_0$ suffer from statistical uncertainties only, which can be characterized by a noise-equivalent absorption coefficient $\alpha_{\mathrm{min}}$. Usually, for the purpose of $\omega_0$ determination, the line profile is measured at several pressures, fitted separately at

*piotr.wcislo@fizyka.umk.pl

 

each pressure, and the $\omega_0(p)$ linear dependence is extrapolated to zero pressure [13–18,20,21]. The goal of this section is to find the optimal pressures at which the profile should be measured to achieve the smallest statistical uncertainty of $\omega_0$.

To keep the considerations relatively simple and general at the same time, we assume that the spectral line shape and, in particular, its width are pressure independent. This condition is well obeyed at low pressures in the Doppler limit, where the line shape can be described by the Gaussian profile. Nevertheless, the analysis presented in this section can also be applied to other cases, when the linewidth only slightly changes over the considered pressure range. In fact, for pressures from 0.3 up to 1.5 atm, at room temperature, the width of the $H_2$ lines may vary by about the factor of 2 from its mean value, but this only slightly influences the conclusion of our analysis. This assumption ensures that the line maximum absorption $\alpha_{\max}$ scales linearly with pressure, hence the signal-to-noise ratio SNR may be written as

$$\mathrm{SNR} = \frac{\alpha_{\max}(p_2)}{\alpha_{\min}}\frac{p}{p_2}, \tag{1}$$

where $p_2$ is some reference pressure. In the simplest case the measurement may consist of two points (see the top panel in Fig. 1). It follows from Eq. (1) that the pressure of the second point $p_2$ should be set to the highest possible value achievable with the spectrometer used. Then the problem reduces to finding the optimal value of $p_1$, which minimizes the uncertainty of the zero-pressure line position $\sigma(\omega_0)$. This should take into account two counteracting effects. On the one hand, higher $p_1$ determines higher SNR [see Eq. (1)]. On the other hand, smaller $p_1$ reduces the uncertainty of the slope of the linear extrapolation. To find a compromise between them, the uncertainty of the zero-pressure line position can be written as

$$\sigma(\omega_0) = \sigma(\omega_2)\frac{1}{|1-\xi|}\sqrt{\xi^{-2}+\xi^2}, \tag{2}$$

where $\xi = p_1/p_2$ and $\sigma(\omega_2)$ is uncertainty of the line position measured at $p_2$. The $\sigma(\omega_0(\xi))$ function is shown in the bottom panel in Fig. 1. Its minimum, corresponding to $\sigma(\omega_0) \approx 4.1\sigma(\omega_2)$, occurs for $\xi = p_1/p_2 \approx 0.46$ (see the gray vertical line). The effective uncertainty $\sigma(\omega_0)$ can be reduced even further if we allow a different number of measurement points at $p_1$ and $p_2$. It can be shown, using a relation similar to Eq. (2), that six times more measurement points at $p_1$ than at $p_2$ ensures the smallest $\sigma(\omega_0) \approx 3.4\sigma(\omega_2)$ at $\xi \approx 0.41$.

The simple analysis presented in this section shows that in the presence of random noise only, the smallest uncertainty is achieved when the measurements are carried out at two pressures $p_1$ and $p_2$, where $p_2$ is the highest possible pressure and $p_1$ is slightly lower than $p_2/2$. Measurements conducted at different pressures would contribute less effectively to the determination of $\omega_0$. In the bottom panel in Fig. 1, we also compare our simulations with the conditions of the available experiments.

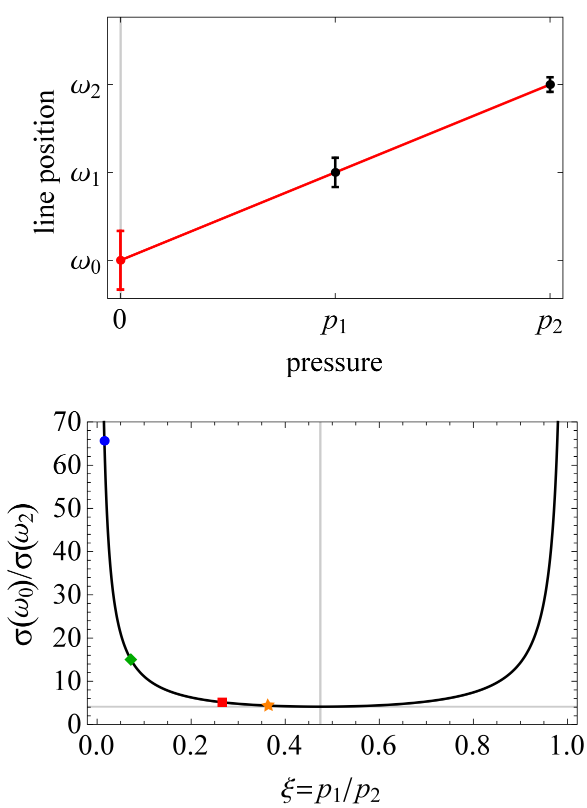


FIG. 1. Shown on top is the simplest scheme of the zero-pressure line position extrapolation, which is adopted in our analysis. The bottom shows the uncertainty of the zero-pressure line position (with respect to the line position uncertainty at $p_2$) as a function of $p_1$ (with respect to $p_2$). The minimum of this function is indicated by the crossing of the gray lines. The symbols show the lowest pressure from the measurements of the $H_2$ $Q(1)$ (2-0) line [20] (blue dot), the $H_2$ $O(2)$ (2-0) line [18] (green diamond), the $H_2$ $S(3)$ (3-0) line [17] (red square), and the $D_2$ $S(1)$ (1-0) line [13] (orange star).

## III. COLLISIONAL EFFECTS

In this section we estimate the magnitude of the systematic error in the determination of the line positions in the Doppler-limited spectroscopy of the rovibrational transitions of $H_2$. The physical origin of this systematic error lies in the incorrectly handled speed dependence of the collisional shift, which leads to asymmetry of the line profile. It should be mentioned that the speed-dependent shift alone would lead to a much larger asymmetry. It is, however, significantly reduced by very frequent velocity-changing collisions. A detailed discussion of this effect is given in Refs. [39,40].

The blue line in the top panel in Fig. 2 shows the shift of the center (defined as the profile maximum) of the $Q(1)$ (1-0) $H_2$ line as a function of density at room temperature. This dependence was generated with the speed-dependent billiard-ball profile [42] with experimental speed dependence [19,43,44] ($\mathrm{SD}_e$BBP). In this profile the velocity-changing collisions are not described by a simple phenomenological model, like soft or hard collisions, but by the approach originating from the $H_2-H_2$ interaction potential [19]. Moreover, the speed dependences of the broadening and shift are derived from their experimental temperature dependence [45]. The relevance of this model for the representation of $H_2$ spectra was validated in Ref. [19]. The red line in Fig. 2 shows the line position versus density determined not from the profile maximum, but from the fit with the symmetric profile. For this propose we used

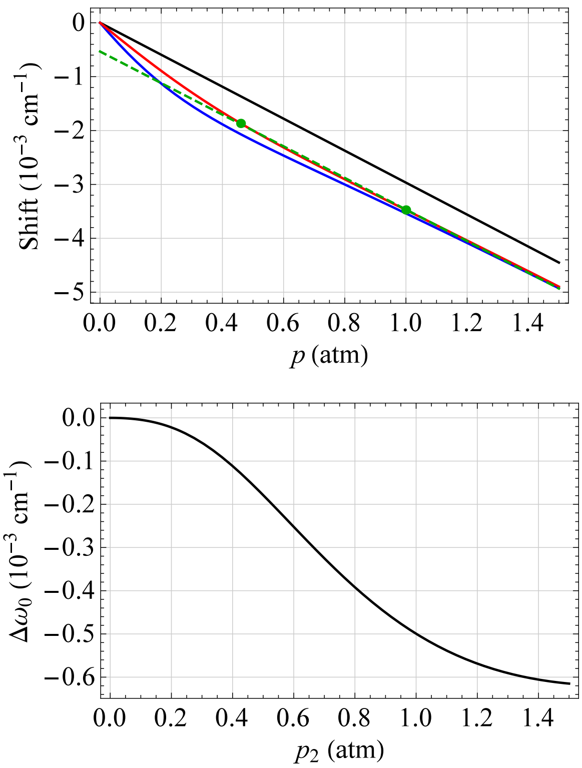


FIG. 2. Shown on top is the nonlinear behavior of the line position as a function of pressure for the case of the $H_2$ $Q(1)$ fundamental line at $T = 296$ K. The green dashed line shows the linear fit to two shifts at $p_2 = 1$ atm and $p_1 = 0.46p_2$ and its extrapolation to zero pressure gives the systematic error of the unperturbed line position. The bottom shows how this error scales with $p_2$, assuming that $p_1 = 0.46p_2$.

the Nelkin-Ghatak [46] and Galatry [47] profiles, in which the speed dependence of collisional broadening and shift is neglected. Both profiles yield almost the same results. The black line in the top panel is the usual linear collisional shift. The nonlinear behavior of the apparent shift results in the systematic error in the line position determination. The green dashed line illustrates this effect for $p_2$ corresponding to 1 atm and $p_1 = 0.46p_2$.

The bottom panel in Fig. 2 shows how the choice of $p_2$ (keeping $p_1 = 0.46p_2$) determines the magnitude of the systematic errors of the line position determination $\Delta\omega_0$. A comparison of this figure with Fig. 1 clearly shows that the determination of optimal values of $p_1$ and $p_2$ requires a compromise between reducing the random and systematic errors. If, for instance, the random noise of the spectrometer at $p_2 \approx 1$ atm corresponds to the uncertainty $\sigma(\omega_2) \approx 10^{-4}$ cm$^{-1}$, then the random-noise contribution to the zero-pressure uncertainty would be $\sigma(\omega_0) \approx 4 \times 10^{-4}$ cm$^{-1}$. On the other hand, it follows from Fig. 2 that the systematic error caused by neglecting the speed dependence of the collisional shift would be $\Delta\omega_0 \approx 5 \times 10^{-4}$ cm$^{-1}$, which means that these conditions are close to optimal. If the random noise at $p_2 \approx 1$ atm would correspond to $\sigma(\omega_2) \approx 10^{-5}$ cm$^{-1}$, then the uncertainty budget would be dominated by the systematic error, which could be reduced by decreasing the value of $p_2$.

## IV. ANALYSIS OF EXPERIMENTAL SPECTRA

In this section we test the influence of the collisional effects on the accuracy of the determination of the unperturbed $H_2$ transitions energies directly from the experimental spectra. For this purpose we reanalyzed the spectra of the $H_2$ $S(3)$ (3-0) overtone from Ref. [17]. The spectra were measured with a cavity ring-down spectrometer, whose absolute frequency scale was achieved by referring to a rubidium calibration line, a technique similar to that demonstrated earlier in Ref. [48].

Fitting the experimental data with complex line-shape models, including the velocity-changing collisions and speed dependence of the broadening and shift, requires determination of several additional parameters. In such a case the parameter describing the speed dependence of the collisional shift is strongly correlated numerically with some other line-shape parameters including the velocity-averaged collisional shift (called for short collisional shift) or the unperturbed transition frequency (line position). This may considerably influence the magnitude of the fitted line asymmetry and the line position. In this analysis we reduce this numerical correlation by applying the multispectrum fitting scheme [49,50]. The experimental spectra from Ref. [17] were collected at 12 pressures from 0.26 up to 0.99 atm (several measurements at each pressure). In Ref. [17] each spectrum was individually fitted with the Galatry profile [47] and then the unperturbed line position was determined from the linear extrapolation of the pressure shift to zero pressure. The line position determined in Ref. [17] is shown in Fig. 3 as a green triangle. In the present work, since the multispectrum fitting procedure is used, we take advantage of only four spectra for each pressure, which is about half of the spectra set from Ref. [17] (other series do not cover the whole pressure range). We test two line-shape profiles, which are based on different models of molecular collisions. The first one is based on a simple phenomenological approach, in which the velocity-changing collisions are described by the hard-collision model [46] and the phase- or state-changing

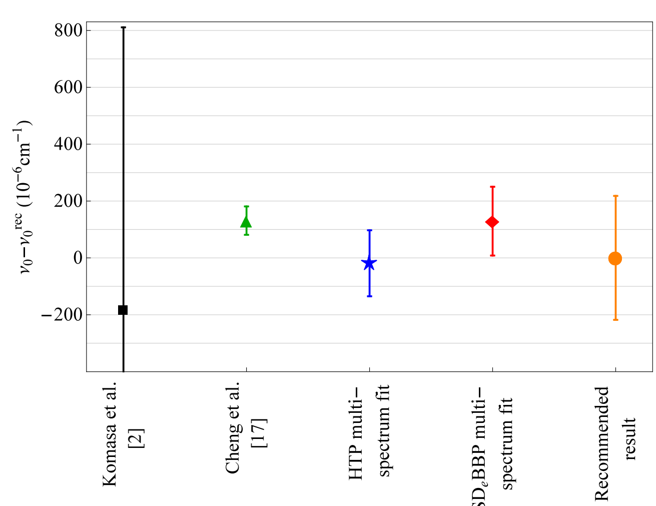


FIG. 3. Comparison of the $H_2$ (3-0) $S(3)$ line position determined from experimental spectra with different approaches; see the text for details. Zero is shifted to the recommended value 12 559.749 39 cm$^{-1}$. The theoretical value calculated by Komasa *et al.* [2] is also depicted.

collisions are handled with a quadratic approximation [51] of the speed dependence of the line broadening and shift. This is a quadratic version of the correlated speed-dependent Nelkin-Ghatak profile given by Pine [52] for which a very effective numerical algorithm was developed by Tran and co-workers [53,54]. To be consistent with the recent International Union of Pure and Applied Chemistry recommendation, we refer to it as Hartmann-Tran profile (HTP) [55]. The zero-pressure line position determined with the HTP multispectrum fit is shown in Fig. 3 as a blue star. Its value corresponds to the mean value determined from the four multispectrum fits (for each measurement series covering all the pressures), while the error bars show the standard deviation. The second profile we adopt in this analysis is the $\mathrm{SD}_e$BBP [19,42] (see Sec. III). We fit all the line-shape parameters, just like in the HTP fits. The corresponding line position and its statistical uncertainty are shown in Fig. 3 as a red diamond. To determine the final value of the line position for the measurement from Ref. [17] and its uncertainty, we considered, beyond the two above approaches, also the line positions determined from the $\mathrm{SD}_e$BBP multispectrum fits for the case with the speed dependence of the broadening and shift fixed to the speed dependence for the fundamental $Q(1)$ line [45] and for the case without speed dependence. For each of these four approaches we calculated the line position and its statistical uncertainty as a mean value and standard deviation, respectively. Depending on the approach used, the standard deviation varied from 5 to $12 \times 10^{-5}$ cm$^{-1}$. We took the largest of these values as our final standard statistical uncertainty. To calculate the final value of the line position, due to the lack of quantitative information indicating which of these four approaches gives the most confident value of the line position, we simply took their mean value. Similarly we used their standard deviation to estimate the systematic uncertainty. However, to take into account that these values may not be representative, we arbitrarily took two standard deviations as a measure of the systematic uncertainty. Hence, the recommended position of the $H_2$ (3-0) $S(3)$ line is $12\,559.749\,39(12)_{\mathrm{stat}}(18)_{\mathrm{syst}}$ cm$^{-1}$, where the numbers in parentheses indicate standard statistical and systematic uncertainties. This value and its standard combined uncertainty (equal to $0.000\,22$ cm$^{-1}$) are depicted in Fig. 3 as the orange circle with error bar.

The deviations between the determinations of the $H_2$ $S(3)$ (3-0) line position with different line-shape models presented in Fig. 3 show that, for the experimental conditions adopted in Ref. [17], the influence of the choice of the collisional line asymmetry model on the line position determination is of the order of $10^{-4}$ cm$^{-1}$ (3 MHz). This conclusion is consistent with the predictions shown in Fig. 2. It demonstrates that the uncertainty budget from Ref. [17] should be complemented by the dominant systematic contribution coming from the oversimplified description of $H_2$ collisions.

In Fig. 4 we compare the magnitudes of various sources of uncertainties, which influence the accuracy of the $H_2$ line position determination, excluding the statistical uncertainty related to the random fluctuations of the absorption strength. Current spectroscopic experiments linked to an optical frequency comb allow the frequency of the probe laser to be determined with an accuracy approaching and even exceeding the kHz level [26,29,56] (see the red bar in Fig. 4). Another source of uncertainty is the asymmetric perturbation of the Doppler-limited profile caused by the relativistic line-shape effects [57–59]. The value of the relativistic systematic shift depends on the hydrogen isotopolog, line frequency, and the approach used to model this effect, but at room temperature it does not exceed a few kHz. Its contribution is depicted in Fig. 4 as a violet bar. It should be emphasized that the relativistic shift does not scale to zero with decreasing pressure. The accuracy of the line position determination is also limited by the uncertainties of the temperature and pressure determination. We tested, by perturbing the measured temperature and pressure, that the line position determined from the multispectrum fit changes by $3 \times 10^{-6}$ cm$^{-1}$ (green bar in Fig. 4) and $8 \times 10^{-6}$ cm$^{-1}$ (orange bar in Fig. 4) due to a temperature change of 1 K and a pressure change of 1%, respectively (note that the linear scaling of all the pressures by the same factor hardly influences the line position, therefore we randomly chose the pressure perturbation from the $\pm 1\%$ range separately for each pressure instead). Both the temperature and pressure can be measured at least one order of magnitude more precisely than we assumed here, hence their influence can be reduced below $10^{-6}$ cm$^{-1}$. Moreover, the pressure uncertainty may be reduced considerably by scaling the pressure-dependent parameters with the profile area instead of scaling with pressure. Finally, as we have shown in the present paper, the systematic uncertainty of the zero-pressure line position caused by the collisional line-shape effects is of the order of $10^{-4}$ cm$^{-1}$ for the physical conditions taken from Ref. [17] (see the blue bar in Fig. 4). It should be mentioned that even if the pressures at which the spectra are collected would be decreased by an order of magnitude, i.e., $p_2 \approx 0.1$ atm (which is experimentally very challenging for such weak lines), then the systematic shift due to collisions would be of the order of $10^{-5}$ cm$^{-1}$ (300 kHz), which still dominates the uncertainty budget from Fig. 4.

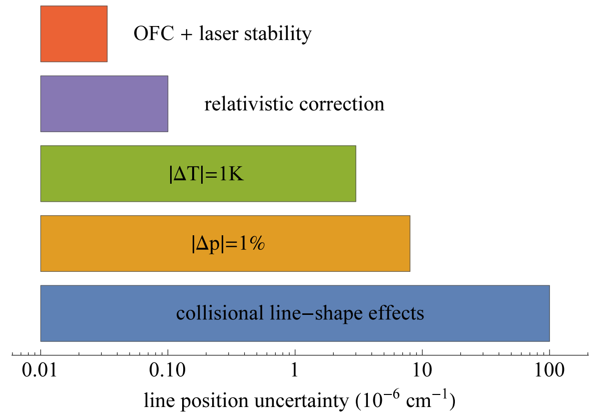


FIG. 4. Systematic contributions to the line position uncertainty budget illustrating the limitations of current Doppler-limited spectroscopy. In practice, the green and yellow bars can be reduced by at least one order of magnitude, since the pressure and temperature can be determined more accurately than the assumed 1% for pressure and 1 K for temperature. It can be clearly seen that the measurements targeted on the $10^{-6}$ cm$^{-1}$ are limited by the collisional line-shape effects.

One may suspect that at the kHz level of accuracy some experimental imperfections also may contribute to the asymmetric deformation of the profile shape and hence introduce additional systematic shift of the line position. Recently, an attempt to estimate the instrumental systematic errors characterizing a cavity ring-down spectrometer was made [60]. However, this problem is beyond the scope of the present paper.

## V. CONCLUSION

In this paper it was shown that the accuracy of current Doppler-limited measurements of the unperturbed frequencies of molecular hydrogen transitions is strongly influenced by the collisional asymmetric line-shape deformation. We estimated the level of the collisional systematic shift, showing that it dominates other sources of systematic uncertainties. It also appears that the uncertainty budgets of the precedent ultra-accurate Doppler-limited measurements of the molecular hydrogen line positions should be revisited.

We question the validity of the widely used assumption that the effective line position, affected by collisions, scales linearly with pressure. Therefore, the zero-pressure line position cannot be determined from a simple linear extrapolation from measurements at higher pressures. Two strategies may be considered to overcome this problem. First, one may reduce the influence of the collisional effects by measuring the spectra at low pressures [26]. However, in contrast to many other molecules, the lines of molecular hydrogen are very weak and cannot by measured with an ultrahigh SNR in the collision-free regime. Therefore, an opposite approach, where the spectra are recorded at higher pressures, but analyzed with a more sophisticated method, should be applied [40,41].

The asymmetry of the line profile is caused by the speed dependence of the collisional shift. However, as shown in Sec. IV, it is difficult to uniquely determine the speed-dependence parameters from the fit (despite the multispectrum fitting being adopted). It is mainly caused by the fact that we simultaneously fit a large number of intercorrelated parameters. As a result, for instance, the fitting routine may nonphysically increase the line asymmetry, artificially changing the line position [61]. It is difficult to quantify this effect without any other information about the collisions. This problem can be resolved by constraining the values of the speed-dependence parameters in the fitting procedure to the values determined either from *ab initio* quantum scattering calculations [40,62–64] or from experimental temperature dependences of the line broadening and shift [19,43,44,65].

The ultra-accurate determination of the transition frequencies in the isotopologs of molecular hydrogen may help answer some of the most intriguing fundamental questions about the existence of new unknown forces [5,6] or the validity of the quantum electrodynamics [10], which is the most accurately tested theory in physics to date. In this paper it was shown that the uncertainty of the line position determination with the Doppler-limited spectroscopy is presently dominated by the collisional deformation of the profile. A proper treatment of these effects should allow the combined uncertainty to be reduced beyond the $10^{-6}$ cm$^{-1}$ level. Hence, Doppler-limited spectroscopy has a potential to be one of the most accurate techniques for studying the $H_2$ transitions.

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