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Recent advances in theoretical calculations of H$_2$ dissociation energies and ultra-accurate measurements of H$_2$ transition frequencies give unprecedented possibilities not only for testing quantum electrodynamics (QED) and relativistic effects, but also for searching new 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, which has not been taken into account in the uncertainty budgets in precedent studies. 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 isotopologues [1–4] open a way for testing relativistic and quantum electrodynamics theories as well as for searching new exotic physics, like 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 narrow line width [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 relatively large line width (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 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 optical frequency comb [33–36]. Even using those techniques such 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 which 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 pres-

sure 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 ω_0 suffer from statistical uncertainties only, which can be characterized by a noise-equivalent absorption coefficient $\alpha_{\min}$. Usually, for the purpose of ω_0 determination, the line profile is measured at several pressures, fitted separately at 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 ω_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 is pressure independent. This condition is well obeyed at low pressures in the Doppler limit, where the line shape can be described by the Gauss profile. Nevertheless, the analysis presented in this section can be also applied to other cases, when the line width only slightly changes over the considered pressure range. In fact, for the 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 assures that the line maximum absorption $\alpha_{\max}$ scales linearly with pressure, hence the signal-to-noise ratio may be written as

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

where p_2 is some reference pressure. In the simplest case the measurement may consist of two points, see the upper 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 used spectrometer. 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 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
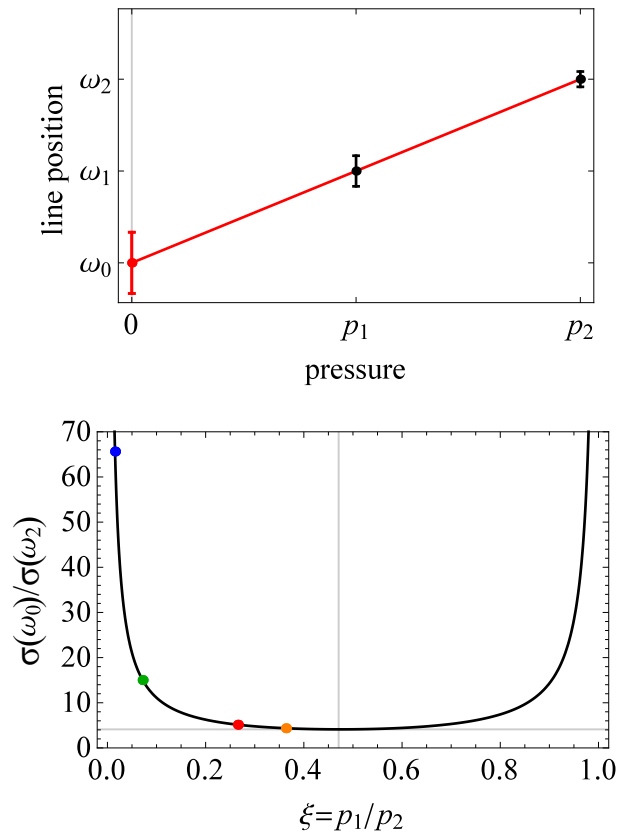

FIG. 1. (Color online) The upper panel shows the simplest scheme of the zero-pressure line position extrapolation, which is adopted in our analysis. The lower panel shows the uncertainty of the zero-pressure line position (with respect to the line position uncertainty at p_2) as a function of p_1 (with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

the lower panel in Fig. 1. Its minimum, corresponding to $\sigma(\omega_0) \approx 4.1 \times \sigma(\omega_2)$, 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 similar relation to Eq. (2), that six times more measurement points at p_1 than at p_2 assures the smallest $\sigma(\omega_0) \approx 3.4 \times \sigma(\omega_2)$ at $\xi \approx 0.41$.

The simple analysis presented in this section shows that in the presence of the 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 smaller than $p_2/2$. Measurements conducted at different pressures would contribute less effectively to the determination of ω_0. In the lower panel in Fig. 1, we also compared our simulations with the conditions of the available experiments.

III. COLLISIONAL EFFECTS

In this section we estimate the magnitude of the systematic error in determination of the line positions in 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].
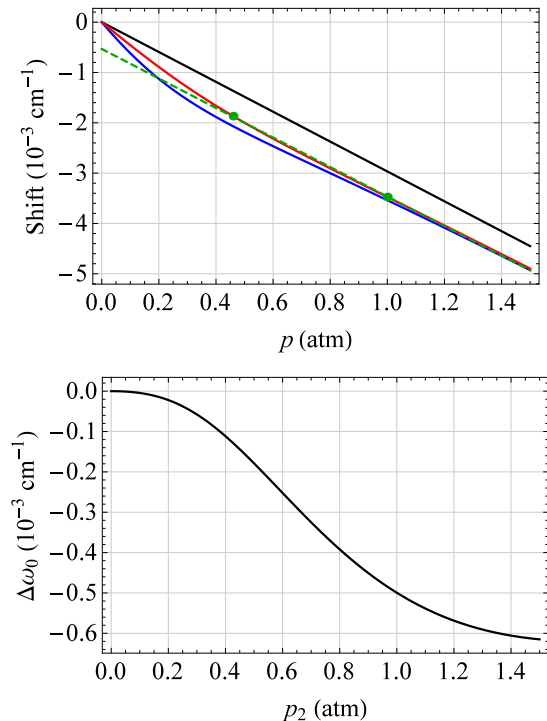
FIG. 2. (Color online) The upper panel shows the nonlinear behavior of the line position as a function of pressure for the case of the H_2 Q(1) fundamental line at $T = 296$ K. The green dashed line shows the linear fit to two shifts at $p_2 = 1$ atm and $p_1 = 0.46 \times p_2$ and its extrapolation to zero pressure gives the systematic error of the unperturbed line position. The lower panel shows how this error scales with p_2, assuming that $p_1 = 0.46 \times p_2$.

The blue line in the upper 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] (SD$_e$BBP). In this profile the velocity-changing collisions are not described by a simple phenomenological model, like soft- or hard-collision, but by the approach originating from the H_2-H_2 interaction potential [19]. Moreover, the speed de-

pendences 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 also shows the line position versus density, but determined not from the profile maximum, but from the fit with the symmetric profile. For this propose we used 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 upper 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 lower 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 $\Delta\omega_0$. Comparison of this figure with Fig. 1 clearly shows that the determination of an optimal values of p_1 and p_2 requires the 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 ringdown spectrometer, which absolute frequency scale was achieved by referring to a rubidium calibration line, a technique similar to that demonstrated earlier in Ref. [48].

Fitting 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 numerically correlated with some other line-shape parameters including the velocity-averaged collisional shift (called shortly collisional shift) or unperturbed transition frequency (line position). This may considerably influence the magnitude of the fitted line asymmetry and the line position. In this
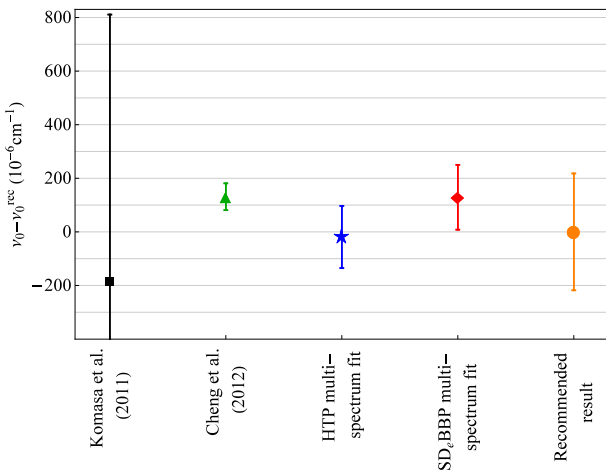
FIG. 3. (Color online) Comparison of the H_2 (3-0) S(3) line position determined from experimental spectra with different approaches, see text for details. Zero is shifted to the recommended value 12559.74939 cm^{-1}. The theoretical value calculated by Komasa *et al.* [2] is also depicted.

analysis we reduce this numerical correlation by applying the multi-spectrum 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 the original paper [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 multi-spectrum fitting procedure is used, we take advantage of four spectra per each pressure only, 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 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 *et al.* [53, 54]. To be consistent with the recent IUPAC recommendation we refer to it as Hartmann-Tran profile (HTP) [55]. The zero-pressure line position determined with the HTP multi-spectrum fit is shown in Fig. 3 as a blue star. Its value corresponds to the mean value determined from the four multi-spectrum 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 SD_eBBP [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

is 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 SD_eBBP multi-spectrum 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 used approach the standard deviation varied from 5 to 12×10^{-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 $12559.74939(12)_{stat}(18)_{syst}$ cm^{-1}, where the numbers in parentheses indicate standard statistical and systematic uncertainties. This value and its standard combined uncertainty (equal to 0.00022 cm^{-1}) is 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 over simplified description of H_2 collisions.

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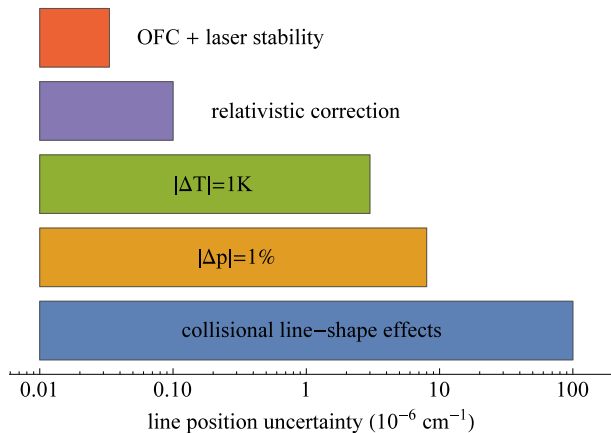
FIG. 4. (Color online) Systematic contributions to the line position uncertainty budget illustrating the limitations of current Doppler-limited spectroscopy. In practice the green and yellow bars can be reduced by at least one order of magnitude, since the pressure and temperature can be determined more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

the uncertainties of the temperature and pressure determination. We tested, by perturbing the measured temperature and pressure, that the line position determined from the multi-spectrum fit changes by 3×10^{-6} cm^{-1} (green bar in Fig. 4) and 8×10^{-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 a 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.

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, the first 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. DISCUSSION AND CONCLUSIONS

In this paper it is 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 ultra-high 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 collisional shift. However, as it is shown in Sec. IV, it is difficult to uniquely determine the speed-dependence parameters from the fit (despite that the multi-spectrum fitting was 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 dependencies of the line broadening and shift [19, 43, 44, 65].

The ultra-accurate determination of the transition frequencies in the isotopologues of molecular hydrogen may help to 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 is 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 re-

duced beyond the 10^{-6} cm^{-1} level. Hence, Doppler-limited spectroscopy has a potential to be one of the most accurate technique for studying the H$_2$ transitions.

ACKNOWLEDGMENTS

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