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H_2, D_2, and HD ionization potentials by accurate calibration of several iodine lines

D. Shiner, J. M. Gilligan,* B. M. Cook,† and W. Lichten
Physics Department, Yale University, Box 6666, New Haven, Connecticut 06511

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In a recent laser spectroscopic study of the H_2, D_2, and HD molecules [J. M. Gilligan and E. E. Eyler, Phys. Rev. A **46**, 3676 (1992)], the energies of transitions between the $X\,{}^1\Sigma_g^+$ ground state and the metastable $EF\,{}^1\Sigma_g^+$ state were measured precisely with respect to seven transitions in the iodine molecule. We report the absolute wavelengths of these iodine transitions with an accuracy of 250 kHz (5 parts in 10^{10}) by interferometric comparison with the iodine-stabilized He-Ne standard at 633 nm. The full accuracy of the transitions to the EF state can now be realized. Improved ionization potentials for H_2, D_2, and HD are obtained using these results in combination with other previous measurements connecting the EF state to high Rydberg states. These ionization potentials are generally, but not completely, in agreement with *ab initio* theory. We also compare our measurements of the iodine wavelengths with less accurate values predicted from previously determined empirical molecular constants of the iodine $B \leftarrow X$ transition. We discuss the possibility of determining these constants more accurately and thereby improving the overall accuracy with which the widely used visible and near-infrared spectrum of I_2 is known.

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I. INTRODUCTION

A precise determination of the ionization potentials of H_2, D_2, and HD provides a sensitive test of the *ab initio* theory of these simplest of neutral molecules. In all recent measurements, this determination is done in two experimental steps. The first step measures the $\sim$12-eV interval between the $X\,{}^1\Sigma_g^+$ ground state and the metastable $EF\,{}^1\Sigma_g^+$ state. The most recent measurement, by Gilligan and Eyler, was accomplished by Doppler-free two-photon absorption of a frequency tripled dye laser [1]. The second step determines the remaining energy to the ionization limit ($\sim$3 eV) by measurement and analysis of EF to high Rydberg state transitions, as reported by McCormack *et al.* [2] for H_2, by Jungen *et al.* [3,4] for H_2 and D_2, and by Gilligan and Eyler [1] for HD.

The frequencies of the $EF \leftarrow X$ transitions measured by Gilligan and Eyler were initially calibrated with respect to nearby iodine absorption lines. There are several reasons why iodine is used to calibrate optical measurements in the visible and near infrared. It has many strong absorption lines in this region of the spectrum, it has a high room-temperature vapor pressure, and it is easy to purify, handle, and keep in sealed optical cells. The frequencies of the Doppler-broadened iodine absorption lines are tabulated in the atlas of the iodine $B\,{}^3\Pi_{0u}^+ \leftarrow X\,{}^1\Sigma_g^+$ transition by Gerstenkorn and Luc [5]. The inherent precision of the hydrogen $EF \leftarrow X$ transitions measured by Gilligan and Eyler, however, exceeded by a factor of 5 the accuracy of the atlas.

To help circumvent this problem, Gilligan and Eyler also used Doppler-free saturated absorption spectroscopy to obtain narrow and precise iodine lines to calibrate their measurements. No atlas exists for the resolved hyperfine spectrum though, and only a few lines have been measured with the required accuracy. Thus, a future experiment was anticipated which would calibrate these lines. We report the results of that experiment. We also discuss the possibility of synthesizing an improved iodine atlas by measuring a number of well-chosen iodine lines. The results would be used to determine the molecular constants that would parametrize the iodine $B \leftarrow X$ spectrum. Our data and analysis suggest that such an approach is reasonable. An improved iodine atlas would result in readily accessible wavelength and frequency references, which would be generally useful for investigations in atomic and molecular spectroscopy, as exemplified by the work in molecular hydrogen discussed here.

II. EXPERIMENT

The experimental arrangement is illustrated in Fig. 1. A frequency-stabilized ($\sim$200-kHz rms) cw dye laser excites iodine transitions in a conventional counterpropagating-beam saturation spectroscopy setup [6,7]. Noise is reduced by amplifying the difference be-

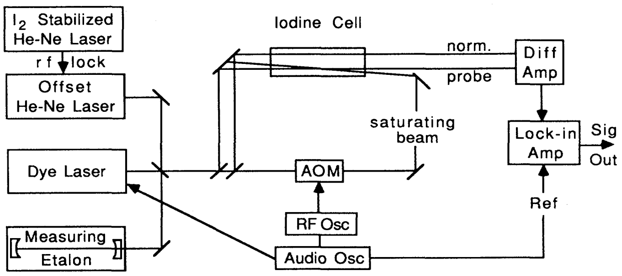

FIG. 1. Schematic of the experimental apparatus for absolute wavelength measurements in iodine. AOM denotes an acousto-optic modulator.

TABLE I. Iodine transition energies compared to previous accurate values.

$^{127}\mathrm{I}_2$ line	Experiment	Frequency (MHz)	Diff. (MHz)
R(47) 9-2*i*	This work	489 880 604.75(0.25)	0.06(27)
(611.8 nm)	Ref. [15][a]	489 880 604.69(0.09)	
P(40) 9-2*o*	This work	489 913 113.11(0.25)	−0.4(1.4)
(611.7 nm)	Ref. [21][b]	489 913 113.50(1.41)	
R(80) 11-2*o*	This work	495 162 602.95(0.25)	0.1(6.0)
(605.4 nm)	Ref. [21]	495 162 602.86(6.00)	
R(66) 13-2*o*	This work	502 019 757.76(0.25)	−0.7(1.1)
(597.0 nm)	Ref. [21]	502 019 758.42(1.02)	

[a] Using the hyperfine splittings from Refs. [16] and [20].

[b] A typographic error in Ref. [21] has this line listed as *R* (40) 9-2*o*.

tween the probe beam and a normalizing beam. The saturating beam was modulated and the consequent variation in intensity of the probe-beam transmission was phase-sensitively detected by a lock-in amplifier to reject further spurious intensity fluctuations.

The iodine cell is 20 cm long and 2 cm in diameter. The cell is kept at room temperature (22±1) °C. The saturating and probe beams are 1 mm in diameter and have powers of 10 and 1 mW, respectively. Typically, for the transitions observed, the absorption of the saturation beam is 30% and the peak-to-peak modulation of the probe beam by the saturating beam is 1−2 %.

The iodine resonances were observed using several slightly different techniques. First, the resonances were observed using the undeflected beam from the acousto-optic modulator as the saturating beam. The dye laser frequencies at the half-maximum points of the lock-in signal were averaged to obtain the resonant frequencies. Next, the first-order diffracted beam from the acousto-optic modulator was used for the saturating beam. This yielded results consistent with the first values, but the size of the background noise was less sensitive to alignment [8]. Finally, we frequency modulated the dye laser and determined line centers from the zero crossings of the lock-in referenced to this modulation. Again, these were consistent with the previous values within our errors (±250 kHz).

The scheme for wavelength measurements is basically the same as that used in previous experiments in hydrogen [9] and helium [10]. A helium-neon laser is offset locked with a tunable rf frequency to an iodine stabilized He-Ne laser at 633 nm. This iodine-stabilized laser [11] has been calibrated with respect to the Cs standard [12] with an accuracy of 1.6 parts in 10^{10}. The dye laser is locked to a measuring étalon which is in turn locked to the offset He-Ne laser. The ratio of the unknown dye laser frequency to the known offset laser frequency is then given by the ratio of their respective order numbers in the measuring étalon. Corrections are made for the curvatures and phases shifts of the étalon mirrors. Details of the method are given elsewhere [13,14]. The wavelength measurements are sufficiently accurate (less than one part in 10^{10}) to contribute negligibly to the error in the iodine measurements.

To help assess the accuracy of the measurements, four previously calibrated iodine lines were remeasured. The agreement with the previous values, as shown in Table I, is quite good, especially 60-kHz agreement with the much-studied line at 611.8 nm [15]. The uncertainty given for our values (250 kHz) is the standard deviation found in measurements taken from day to day. Rather than taking the error in the mean, we used this more conservative estimate since the source of these variations was not determined. Effects due to iodine temperature and pressure, laser intensity, and iodine line shape are not expected at this level [16] and were not observed.

TABLE II. Measured wave numbers of the iodine lines used to calibrate the H_2, D_2, and HD transitions.

$^{127}\mathrm{I}_2$ line	I_2 atlas number in Ref. [5]	Energy (cm^{-1})
R(73) 11-2*i*	3286 [H_2 *Q*(0) calibration]	16 527.288 442(8)
R(79) 11-2*u*	3247 [H_2 *Q*(1) calibration]	16 518.395 407(8)[a]
R(9) 11-2*r*,*s*	3652 [D_2 *Q*(0) calibration]	16 576.909 149(8)[b]
R(24) 13-3*a*	3603 [D_2 *Q*(1) calibration]	16 572.228 998(8)
R(40) 11-2*o*	3515 [D_2 *Q*(2) calibration]	16 563.111 924(8)
P(49) 11-2*i*	3417 [HD *Q*(0) calibration]	16 550.166 120(8)
P(114) 12-2*o*	3374 [HD *Q*(1) calibration]	16 543.515 471(8)

[a] This line was incorrectly identified as the *o* hyperfine component in Table IV of Ref. [1].

[b] The reproducibility of this line did not seem to be affected by the accidental close overlap of a weak and strong hyperfine component.

TABLE III. $EF \leftarrow X$ transition energies in H_2, D_2, and HD. Results of Gilligan and Eyler [1], combined with Table II.

Transition	Energy (cm^{-1})
H_2 $Q(0)$	99 164.782(3)
H_2 $Q(1)$	99 109.727(3)
D_2 $Q(0)$	99 461.440(3)
D_2 $Q(1)$	99 433.710(3)
D_2 $Q(2)$	99 378.387(2)
HD $Q(0)$	99 301.340(3)
HD $Q(1)$	99 259.912(3)

III. RESULTS AND DISCUSSION

Table II gives the results for the wave numbers of the seven iodine lines used as references for the $EF \leftarrow X$ state transitions in H_2, D_2, and HD. These values allow the absolute frequencies of the $EF \leftarrow X$ state transitions of Gilligan and Eyler [1] to be improved by a factor of 5. These $EF \leftarrow X$ state transitions energies are given in Table III. The contribution of the iodine calibrations to the $EF \leftarrow X$ state transition uncertainties, instead of dominating, now contributes only 1.5 MHz out of 90 MHz. Considerable further improvement in the molecular hydrogen measurements is now possible without limitations due to wavelength calibration.

The ionization potentials of H_2, D_2, and HD can be obtained by combining the $EF \leftarrow X$ transition values of Table III with measurements and analyses of transitions from the *EF* state to high Rydberg states. Ionization potentials obtained in this way are given in Table IV and compared with *ab initio* theory. The uncertainty in the energy interval from the *EF* state to the ionization limit now dominates the errors in the ionization potentials. The theoretical values for the ionization potentials given in Table IV are the results of new *ab initio* calculations by Kolos and Rychlewski [17]. We note that care must be taken when comparing these theoretical results to the previous ones. Kolos informs us [18] that the previous values for the binding energies of H_2, D_2, and HD, based on the *ab initio* calculations by Kolos, Szalewicz, and Monkhorst [19], must be corrected by 0.065, 0.016, and 0.041 cm^{-1}, respectively, because incorrect values for nonadiabatic corrections were used in that work.

The agreement between the new theory and experiment is generally impressive, especially considering that the differences between the *ab initio* and measured values are much smaller than the relativistic and radiative contributions to the ionization potentials (around 1 and 0.4 cm^{-1}, respectively). Nonetheless, a potential problem exists in the three-standard-deviation discrepancy between the theoretical value of the ionization potential of H_2 and the measured value obtained by combining the Rydberg state measurements by McCormack *et al.* [2] with the improved *EF* state energies reported here. The dominant contributions to the uncertainties of the theoretical values are in the relativistic and radiative terms, which vary only slightly from one isotopic species to another. This suggests a possible experimental problem. On the other hand, the dominant experimental uncertainties are not isotopically dependent, and the variation with mass between the calculated and measured values, though on the order of experimental uncertainty, is consistent with an isotope shift not accounted for by theory. More accurate theoretical and experimental work would be needed to clarify this situation.

Given the widespread use of iodine to calibrate optical measurements in the visible and near infrared (500–900 nm), overall improvements in the knowledge of the iodine line positions would be quite useful. We note that Gerstenkorn and Luc [5] were able to compute, within the measurement errors of ±60 MHz, the positions of the ~100 000 lines listed in their atlas with the use of only 46 molecular constants. Using these constants and constants which describe the hyperfine structure of iodine [20], we computed the expected positions of the iodine lines we measured. One would expect the original 60-MHz fluctuations of the atlas to be smoothed out by the fit, and this was the case. The results appear in Table V. Within the 11-2 rovibrational band, the discrepancies are slowly increasing with increasing angular momentum, and are quite well behaved. Changes in the upper vibrational level result in less-predictable deviations of the order of 10 MHz, and the lone value involving a change in the lower vibrational number has a deviation of ~40 MHz. Comparisons with previous accurate calibrations lead to similar observations [5,21].

These observations encourage us to suggest that measurements of a few hundred appropriately chosen Doppler-free iodine wavelengths could result in a calibration of the full iodine spectrum in the visible and near in-

TABLE IV. Ionization potential of H_2, HD, and D_2 (cm^{-1}).

Species	Ionization potential	*Ab initio* theory	Diff.
H_2	124 417.507(12)[a]	124 417.471[b]	+0.036(12)
	124 417.484(17)[c]		+0.013(17)
HD	124 568.481(12)[d]	124 568.465[b]	+0.016(12)
D_2	124 745.353(24)[e]	124 745.377[b]	−0.024(24)

[a] Reference [2] and Table III.
[b] Reference [18].
[c] Reference [3], Table III, and Ref. [24].
[d] Reference [1] and Table III.
[e] Reference [4], which uses the results given in Table III.

TABLE V. Difference between predicted and measured iodine frequencies. Constants for the hyperfine splittings are obtained using the empirical formulas of Ref. [20]; rotational-vibrational splittings are obtained using the molecular constants of Ref. [5].

$^{127}I_2$ line	Difference (MHz)
$P(40)$ 9-2o	45.6
$R(47)$ 9-2i	47.4
$R(9)$ 11-2r,s	34.2
$R(40)$ 11-2o	37.6
$P(49)$ 11-2i	36.9
$R(73)$ 11-2i	40.5
$R(79)$ 11-2u	41.2
$R(80)$ 11-2o	41.5
$P(114)$ 12-2o	32.1
$R(66)$ 13-2o	41.6
$R(24)$ 13-3a	7.5

frared with greatly improved (to less than 1 MHz) accuracy. We note that the ground state of iodine is very well isolated from excited-state perturbations and a single potential curve should remain adequate for describing the relevant ground-state rotational and vibrational levels to less than 1 MHz. However, the B state is not so well isolated [5,22,23]. At the 1-MHz level, more than a few hundred well-chosen data points might be required to yield an adequate parametrization of the relevant rotational and vibrational levels.

The hyperfine splittings of iodine must also be considered. They are predicted to ~ 100 kHz by iodine's quadrupole moment constant and spin-orbit constant. Slow variations in these two constants with rovibrational level would need to be known somewhat more accurately than they are now [20]. This effort could be avoided, or at least minimized, by calibrating particular hyperfine components of the line, for example the component i when J'' is odd, and the component f when J'' is even. These components have angular momentum J equal to the total angular momentum F, which leads to a much reduced spin-orbit contribution (generally <1 MHz). These components also have small quadrupole eigenvalues, which puts them nearer the center of the unperturbed line and makes them less sensitive to the value of the quadrupole moment constant.

To summarize, our measurements allow the full accuracy of recent measurements of $EF \leftarrow X$ transitions in molecular hydrogen and its stable isotopes to be realized. Improved ionization potentials, obtained in combination with other measurements, are in general, but not complete, agreement with *ab initio* theory. The measured iodine lines are calibrated with sufficient accuracy to allow for a great deal more precision in the hydrogen $EF \leftarrow X$ transitions. An improved calibration of the entire iodine visible and near-infrared spectrum seems feasible, but would require new measurements of at least several hundred well-chosen lines.

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*Present address: Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303.

†Present address: Physics Department, California Institute of Technology, Pasadena, CA 91125.

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