the shapes of the complex components in Figure 4 differ appreciably from those in Figure 3 where the differences in intrinsic line width are to a large extent masked by the effects of saturation. It is noted that the line shape of these complex lines is extremely sensitive to slight differences in the widths of the components as is particularly seen by comparing both the experimentally observed and simulated shapes of the second group of ¹³C lines in Figure 3 and 4. In Figure 4 the ¹³C structure of the central lines is dominated by the hyperfine constant of the radicals having ${}^{13}C$ at C_2 so that $a_C(C_2)$ can be determined from detailed analysis of the experiments at low power to be 1.46 G (i.e., ± 0.02 G). The fact that the lines with ¹³C at C₁ are appreciably broader than the other components implies that there is a high degree of anisotropy at this position.

The ¹³C hyperfine constants noted here are closely related to those reported by Rieger et al.¹⁰ for the terephthalonitrile radical anion in N,N-dimethylformamide solution as determined in electrochemical experiments ($a_{\rm H} = 1.59$ G, $a_{\rm C}({\rm C}_1) = 8.81$ G, $a_{\rm C}({\rm C}_2) = 1.98 \text{ G}, a_{\rm N} = 1.81 \text{ G}, \text{ and } a_{\rm C}({\rm CN}) = 7.83 \text{ G}$). The values of $a_{\rm H}$ and $a_{\rm C}({\rm C}_2)$ are very similar and clearly indicate similar unpaired spin distribution on the ring of the two radicals. The observed proton hyperfine constant (-1.52 G) indicates, from the McConnell relationship¹¹ with $Q_{\rm H} = -25$ G, that ρ_2 , the unpaired spin population at C₂, is 0.06. This value is similar to the estimate of 0.067 for ρ_2 in the terephthalonitrile radical anion.¹² From the Karplus-Fraenkel relation,¹³ since $\rho_3 = \rho_2$, the hyperfine constant of the carbon at C₂ should be described by

$$a_{\rm C}({\rm C}_2) = (Q_1 + Q_a)\rho_2 + Q_a\rho_1 \tag{1}$$

where ρ_1 is the unpaired spin population at C₁ and Q_1 and Q_a are σ - π parameters relating the observed ¹³C coupling to the contributions resulting from π spin population on the local and adjacent atoms. Q_1 and Q_a are found in other systems to be respectively ~28 and $-10 \text{ G}.^{14}$ Since ρ_2 is small (0.06), the con-

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tribution of the first term in eq 1 (1.1 G) is less than the observed splitting (1.46 G). Application of the Karplus-Fraenkel relation, therefore, indicates that ρ_1 must be either 0.26 or -0.04, depending on whether $a_{C}(C_{2})$ is negative or positive. The latter choice would place essentially all of the unpaired spin population on the carboxyl groups and is unrealistic so we conclude that the sign of $a_{\rm C}({\rm C}_2)$ must be negative and that ρ_1 is ~0.26. These values place ~76% of the unpaired spin on the ring, indicating that $\sim 12\%$ is on each of the carboxyl groups. Similar conclusions for the terephthalonitrile radical anion were reached by Reiger and Fraenkel from considerations of the magnitude of the ¹³C splittings observed in that case. We note here that the observation that the lines of the radicals labeled at C_1 are more anisotropic than the other lines is in accord with the high local spin population at this position.

From the unpaired spin on the ring, one predicts from the Karplus-Fraenkel relationship that $a_{\rm C}({\rm C}_1)$ should be ~5.8 G. The smaller value observed here (4.64 G) and the larger value in the case of the terephthalonitrile radical anion (8.8 G) presumably reflect differences derived from unpaired spin on the adjacent CO₂⁻ and CN groups. The contribution to $a_{\rm C}$ from spin on adjacent carboxyl groups ($Q_a(CO_2) = -10$ G) is, therefore, comparable to that on other adjacent carbon atoms. The larger value for $a_{\rm C}({\rm C}_1) = 8.81$ G noted by Rieger et al. for terephthalonitrile anion implies that Q_a derived from unpaired spin on the CN group is positive and of the magnitude of ~ 15 G.

Eiben and Schuler⁵ found in studies of carboxylated cyclohexadienyl radicals that the carboxyl ¹³C hyperfine constant probed the unpaired spin population on the adjacent ring carbon atoms in much the same way as the proton values, i.e.

$$a_{\rm C}({\rm CO}_2^-) = Q({\rm CO}_2^-)\rho \tag{2}$$

where $Q(CO_2^{-})$ can be taken as ~15.8 G. This relation breaks down in the present case where the observed value for $a_{\rm C}({\rm CO_2}^-)$ = 1.4 G is much smaller than the \sim 4 G predicted. It is clear from this that in the present case a contribution must be added to eq 3 to take into account the significant population of unpaired spin on the carboxyl group and that this contribution must be of opposite sign to that derived from spin on the ring carbon.

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Accurate Measurement of Vibrational Transition Energies for a Wide Range of v, J States Using CARS Spectroscopy of Chemical Reaction Products: Spectroscopy of H₂ from the H + HI Reaction

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 $Q_v(J)$ transition energies of H₂ are measured for v = 0-4, J = 0-18 by coherent anti-Stokes Raman scattering (CARS) spectroscopy of rovibrationally excited H₂ from the H + HI \rightarrow H₂ + I reaction at high collision energies. The accuracy of the measurements reported here is 0.05 cm⁻¹, limited by the bandwidth of the laser sources used. The measured transition energies generally agree with those predicted by ab initio quantum calculations and with previous less precise measurements based on H₂ electronic spectroscopy. However, discrepancies outside mutual uncertainties are common, and the accuracy of the ab initio calculations appears to be somewhat less than the 0.015 cm⁻¹ claimed. Measurements with an accuracy of 0.0005 cm⁻¹, much greater than that of the present measurements, are possible with the methods described here by using narrow-bandwidth laser sources for CARS spectroscopy.

Introduction

In a recent publication,¹ Nieh and Valentini reported the use of coherent anti-Stokes Raman scattering (CARS) spectroscopy to obtain spectra of high v, J states of photofragments under

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of the Q-branch transitions involving these v, J states. The high collision energy, 1.6 eV, and the large excergicity of the reaction, 1.4 eV, allow the population of otherwise inaccessible rovibrational states of H_2 , and consequently the measurement of the energies of otherwise inaccessible transitions. In the present experiments we have detected H_2 in over 35 rovibrational states up to v = 4and J = 18, with rovibrational energies as high as 19800 cm⁻¹.

Being the simplest molecule, H_2 is a prototype for theoretical and experimental study of molecular structure and spectroscopy. There has been much effort devoted to obtaining a complete, first principles, theoretical description of this molecule, particularly the structure and spectroscopy of the electronic ground state.²⁻ In particular, recent calculations^{6,7} have produced very extensive rotational- and vibrational-state eigenenergies for the ground electronic state with purported accuracy of 0.015 cm⁻¹. The spectroscopy of H_2 in its ground electronic state is of considerable importance beyond the realm of molecular spectroscopy and quantum mechanics. As the most abundant molecule in the universe, it provides astrophysicists with a probe of the physical conditions in remote parts of the universe through its emission spectrum. Astrophysical interest in H₂ rovibrational spectroscopy is evidenced by the observation of pure rotational transitions of molecular hydrogen in the Orion Nebula.^{13,14}

Raman spectroscopy provides a convenient method for the accurate determination of rovibrational transition energies in molecular hydrogen. Recent Raman measurements have been reported both to test the ab initio quantum calculations and to provide the spectroscopic data necessary to interpret astrophysical spectroscopic measurements.^{8,12} These Raman measurements agree with the ab initio calculations to within expressed uncertainties. However, they include only a limited number of transitions involving only the lowest vibrational and rotational levels of H₂, v = 0 and $J \le 9$. It should be possible to access a greater number of higher rovibrational states of H₂ by studying a thermally populated sample at high temperature, but this avenue is as yet unexplored fully.12

Dabrowski¹¹ has used electronic emission spectroscopy of H₂ to access high v, J states, measuring a great number of lines in the Werner and Lyman bands of H_2 in a flash discharge experiment. She has calculated many H_2 ground-state vibrational and rotational energy levels for $v \le 14$ and $J \le 30$ from these results. Her experimentally derived rotational and vibrational eigenenergies are in general agreement with the theoretical predictions. However, there are some discrepancies between the measured and calculated lines, and the experimental energy levels have considerable uncertainty, ± 0.1 cm⁻¹.

Experiment

Rovibrationally excited H_2 from the $H + HI \rightarrow H_2 + I$ reaction is observed in this experiment using coherent anti-Stokes Raman scattering (CARS) spectroscopy. The CARS apparatus used in this experiment has been described previously¹ and has been modified only by the addition of a Ta/Ar hollow cathode lamp (HCL) used to obtain the spectrum of argon as a wavelength reference for the tunable dye laser. The apparatus, shown in Figure 1, employs a Quanta-Ray Nd:YAG DCR-2A as the sole source of laser light. The Q-switched 1064-nm output of the Nd:YAG is doubled in a Quanta-Ray harmonic generator (HG II) and provides 532-nm light in 7-ns pulses at a rate of 10 Hz

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Figure 1. Schematic diagram of the apparatus used to obtain CARS spectra of H_2 from the H + HI \rightarrow H_2 + I reaction.

with a line width of ~ 0.3 cm⁻¹. Twenty-five millijoules of the Nd:YAG second harmonic is split off and used as the pump beam $(\omega_{\rm p})$ in the CARS process; 180 mJ is channeled to pump a Quanta-Ray pulsed dye laser (PDL-2) which provides 8-25 mJ of tunable visible laser light. The output of the PDL-2 is used as the Stokes beam (ω_s) in the CARS process. Eighty millijoules of the Nd:YAG second harmonic is doubled in a Quanta-Ray wavelength extender (WEX-1) and provides 16 mJ of 266-nm UV light, which is used as the dissociation beam (ω_d) in the experiment.

The three beams are combined with dichroic mirrors and focused into the reaction region, a 1-cm³ cell suspended in a 7-L reaction vessel. The beams are precisely overlapped spatially and have coincident foci. The beams are focused to a beam waist of \sim 100 μ m to achieve the high-power densities necessary for the CARS process. Delay lines are adjusted so that the $\omega_{\rm p}$ and $\omega_{\rm s}$ pulses are temporally overlapped and delayed with respect to the arrival of the ω_d at the cell by 3.5 ns. HI is flowed into the reaction cell at a rate of ~ 0.03 Torr-L s⁻¹, and argon is flowed from either end of the reaction vessel as a buffer gas to aid in keeping reaction products from collecting on the vessel windows. The gas flow rates are set to ensure renewal of the contents of the reaction cell between laser shots. The total pressure in the vessel is held constant at 10 Torr.

Translationally hot hydrogen atoms are produced when ω_d dissociates HI to give H and I. In the 3.5 ns between ω_d and the arrival of ω_s and ω_p the 1.6-eV H atoms produced from the photodissociation collide with the remaining undissociated HI. A fraction of such collisions are reactive, producing rovibrationally excited H_2 via

$$H + HI \rightarrow H_2^* + I \tag{1}$$

Product H₂ is detected by CARS spectroscopy using ω_p and ω_s via the doubly degenerate three-wave mixing CARS process to generate ω_{as} , the anti-Stokes signal beam

$$\omega_{\rm as} = 2\omega_{\rm p} - \omega_{\rm s} \tag{2}$$

After exiting the reaction vessel the collinear beams are recollimated, and beam-splitting optics separate ω_d , ω_s , and ω_p from ω_{as} . The signal beam is then filtered through a double monochromator and directed into an RCA 1P28 photomultiplier tube (PMT). The output of the PMT is processed through a boxcar averager. A CARS spectrum of H₂ is generated by scanning ω_s through Raman

resonances at $\omega_r = \omega_p - \omega_s$ and detecting the intensity of ω_{as} . A Fisher Scientific Ta/Ar hollow cathode lamp (HCL) is configured to receive the ω_s beam reflected from the back of the $\omega_{\rm p}/\omega_{\rm s}$ dichroic mirror. The HCL output is processed through a second SRS gated boxcar averager. This allows the acquisition of the optogalvanically detected Ar absorption spectrum.¹⁶ A

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TABLE I: Energies of Hydrogen Q-Branch Transitions (cm⁻¹) Measured by CARS Spectroscopy of H_2 from $H + HI \rightarrow H_2 + I$



Figure 2. Differences between the measured and calculated⁷ values of the v = 0 Q-branch transition energies of $H_2(X^1\Sigma^+_g)$ for J = 7-19 (cm⁻¹). Circles represent measurements obtained in this work. Triangles represent measurements presented by Dabrowski.¹¹

dual-channel strip chart recorder is employed to record the boxcar processed signals from both the HCL and the CARS apparatus simultaneously.

Once the spectra are obtained, the argon absorption lines are assigned by using the tabulation of Striganov and Sventitski.¹⁵ These tables provide most of the Ar line positions to 0.01-cm⁻¹ accuracy or better. With the Ar lines as standards in the calibration the ω_s positions of the H₂ spectral lines are measured by direct interpolation from the identified Ar absorption positions. In several cases the positions of the H₂ lines were measured repeatedly, relative to different pairs of Ar absorptions. This reproduced the ω_s H₂ positions reliably to within 0.05 cm⁻¹, which we take to be the uncertainty in our experiment. The frequency of $\omega_{\rm p}$, although constant in the experiment, must be established accurately in order to calculate the energies of the observed transitions. In order to find the ω_p frequency in the experiment, the established^{8,9} energies of the Q-branch transitions accessible in a 298 K thermal distribution of H_2 are used. The reaction vessel is filled with 6 Torr of static, 298 K H₂, and a CARS spectrum of the thermally populated sample is taken. The ω_s frequency is determined, as above, for established Q-branch transition energies, v = 0, J = 0-5, and ω_p is given by the relation

$$E(v',J' \leftarrow v,J) = \omega_{\rm p} - \omega_{\rm s} \tag{3}$$

Once the constant ω_p frequency is determined, the remaining observed transition energies for which ω_s is calibrated can be calculated via eq 3.



Figure 3. Differences between the measured and calculated⁷ values of the v = 1 Q-branch transition energies of $H_2(X^1\Sigma^+_g)$ for J = 9-17 (cm⁻¹). Circles represent measurements obtained in this work. Triangles represent measurements presented by Dabrowski.¹¹



Figure 4. Differences between the measured and calculated⁷ values of the v = 2 Q-branch transition energies of $H_2(X^1\Sigma^+_g)$ for J = 3-13 (cm⁻¹). Circles represent measurements obtained in this work. Triangles represent measurements presented by Dabrowski.¹¹



Figure 5. Differences between the measured and calculated⁷ values of the v = Q-branch transition energies of $H_2(X^1\Sigma^+_g)$ for J = 1-13 (cm⁻¹). Circles represent measurements obtained in this work. Triangles represent measurements presented by Dabrowski.¹¹

Results

In Table I we present the energies of the $Q_v(J)$ transitions of H_2 measured in this study. It should be noted that the higher transitions presented here, v = 0, J = 7-18 and v = 1-4, J = 4-17, represent states as yet unattainable from a thermal hydrogen population and so speak of the usefulness of the methodology described here.

Figures 2-5 contain plots of the differences between the transition energies measured in this work and those calculated from the best available ab initio potential for H_2 .⁷ Also shown in Figures 2-5 are the differences between the calculations and the transition energies determined by Dabrowski,¹¹ for Q₀- $(J)-Q_3(J)$, respectively. It should be noted that since the uncertainty in the energy levels measured by Dabrowski¹¹ is 0.1 cm⁻¹,

⁽¹⁶⁾ Downey, S. W.; Nogar, N. S. Appl Spectrosc. 1984, 38, 876.

the uncertainty for the energy of transition between these levels is 0.14 cm^{-1} .

Discussion

It is clear from Figures 2–5 that the two experimental measurements agree with one another within mutual uncertainties, the rms deviation between them is 0.205 cm^{-1} , while the uncertainties are $\pm 0.05 \text{ cm}^{-1}$ for the present data and $\pm 0.14 \text{ cm}^{-1}$ for the data of Dabrowski. The agreement between our experimental measurements of the transition energies and the values obtained from ab initio calculations is generally good, the rms deviation being just 0.155 cm⁻¹, with the measured values being higher on average. However, this rms deviation is considerably larger than would be expected, since the claimed uncertainty in the vibrational-rotational eigenenergies is only $\pm 0.015 \text{ cm}^{-1}$, and then the uncertainty in the transition energies is only $\pm 0.021 \text{ cm}^{-1}$.

The Q-branch transition energy measurements for the v = 1-3 states agree with the calculations reasonably well to within statistical expectation, given the presented error bars. However, the v = 0 data show less agreement than the upper state transitions. Our measured transition energies for $Q_0(J)$ are systematically higher than the calculated values. On the average the measured values are 0.2 cm⁻¹ higher. It is not clear why. Further more accurate measurement of these transition energies may be warranted to eliminate or clarify these discrepancies.

While our measurements generally confirm the accuracy of the calculations, the uncertainty presented for the calculated eigenenergies, 0.015 cm^{-1} , is clearly too small. A more realistic value is $\pm 0.042 \text{ cm}^{-1}$. While larger than the claimed uncertainty in the calculations, we hasten to add that this is still a remarkably small error for a purely ab initio structure calculation. The measurements reported here probably confirm the calculated values to an accuracy suitable for astrophysical spectroscopic uses. We note that much more precise determination of the H₂ Q-branch transition energies can be achieved using the methodology described here. These measurements can be carried out with an uncertainty of 0.0005 cm^{-1} by implementation of pulse-amplified single-frequency dye lasers for use in CARS spectroscopy. With this degree of precision a definite comment on the state of the calculations can be made.

There are ways in which this experiment can be further improved. The 266-nm dissociation beam produced H atoms by the photodissociation of HI with 1.6-eV translational energy. This collision energy and the 1.4-eV exoergicity allow the H₂ product to be formed in states up to v = 6. However, due to the chemical dynamics of the system, only vibrational states up to v = 4 were detectable. In the reaction, H₂ was not produced in low rotational states in low vibrational states in detectable quantities, again due to restrictions imposed by the chemical dynamics of the system. In the case of the v = 0 low rotational states, J = 0-5, this could be overcome by substituting a thermally populated sample of H_2 , but in the v = 1 and v = 2 states the low-rotational-state Q-branch line positions could not be measured. Generation of 1.6-eV H atoms leads to $H + HI \rightarrow H_2 + I$ production of H_2 over a wide range of rotational and vibrational states, but it is highly likely that generation of H atoms with higher and lower energies than this value could provide coverage of an even wider range of H₂ product states. With photolysis wavelengths from 310 to 190 nm H atom energies of 0.94-3.5 eV are possible.

The populations of H_2 states of even J are a factor of 3 less than the populations of adjacent odd-J states due to the nuclear spin statistics of H_2 . This made the line positions of the Q-branch transitions involving even-numbered J states of H_2 difficult to measure, especially for rotational states already disfavored by the reaction dynamics. The manifestation of this spin statistics effect is most evident in the v = 3 low-J and v = 4 measurements, where the even-J-state transitions are absent. Generation of H atoms over a finite energy range could offset this difficulty by providing some control of the H_2 product distribution. We should also point out that it might be possible to broaden the rotational distribution of the detected H_2 somewhat by allowing the nascent product distribution from the reaction to relax. Our present experiments are designed for study of reaction dynamics under single-collision conditions, and hence have been set up taking care to eliminate such relaxation. Within the limits of the current design of the CARS apparatus it is not possible to measure products under conditions of significant relaxation.

One characteristic of the CARS process that is of interest for this work is that the signal level is a measure of the difference in the populations of the upper and lower states connected by the Raman transition. Consequently, transitions involving states of equal populations exhibit no signal. In the $H + HI \rightarrow H_2 + I$ reaction at 1.6 eV the H_2 product distribution is such that there are almost equal populations in v = 0, J = 13 and v = 1, J = 13as well as for states of the same J in the v = 1 and v = 2 states, for J of 3-8. It can be seen in Table I that the transitions involving these states, $Q_0(13)$ and $Q_1(3-8)$, were thus undetectable in this study. Once again, generation of H atoms with different energies can be expected to eliminate such difficulties by altering the H_2 product distribution.

Pursuit of experiments like that described here can provide extensive and accurate data on the H₂ molecule. However, it is significant to note that the usefulness of this methodology is not limited to H₂ alone. This method can be applied to elucidate the spectroscopy of any system involving the production of Ramandetectable excited species. Photodissociation,¹ reactive collisional excitation (i.e., H + HI \rightarrow H₂ + I), and inelastic collisional excitation (i.e., H + AB \rightarrow H + AB(v,J)) are general methods of producing broad distributions of vibration-rotation states, in many cases up to the dissociation limit, so the approach described here is one that should prove useful in the spectroscopic study of many diatomic and polyatomic molecules. Given current technology in narrow-bandwidth laser sources, very high resolution spectroscopic information on such highly excited rovibrational states is within easy reach.

Summary

We have shown that it is possible and efficient to measure vibrational Q-branch transition energies of H₂ by producing a wide range of rovibrationally excited states of H₂ from the reaction of translationally hot H atoms with HI and detecting the products via CARS spectroscopy. The measurements reported here, for transitions involving v = 0-3, J = 0-18, have generally confirmed the results of the ab initio calculations of H₂ rotational and vibrational eigenenergies by Schwartz and LeRoy.⁷ However, the uncertainties quoted by them, ± 0.015 cm⁻¹, seem too small and are more likely to be ± 0.042 cm⁻¹. Even at this level of accuracy the calculations represent an impressive accomplishment of ab initio quantum chemistry. By accessing a wide range of H atom energies through HI photolysis between 190 and 310 nm, it should be possible to generate H_2 in the electronic ground state in all of the rotational and vibrational energy states below 3.5 eV. This would allow access of states up to v = 8 and J = 26. By use of pulse-amplified single-frequency dye lasers it should be possible to determine the line positions of the H₂ Q-branch transitions between states in this set to ± 0.0005 -cm⁻¹ uncertainty. Even further, this very powerful methodology can be implemented to obtain such accurate spectroscopic information on a vast number of diatomic and polyatomic molecules. Current discrepancies between the measured and calculated transition energies of H₂ warrant further more precise and more complete measurement of the H₂ Q-branch transition energies.

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