The $D^1\Pi_u$ state of HD and the mass scaling relation of its predissociation widths

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Abstract

Absorption spectra of HD have been recorded in the wavelength range of 75–90 nm at 100 K using the vacuum ultraviolet Fourier transform spectrometer at the Synchrotron SOLEIL. The present wavelength resolution represents an order of magnitude improvement over that of previous studies. We present a detailed study of the $D^1\Pi_u$–$X^1\Sigma_u^+$ system observed up to $v' = 18$. The $Q$-branch transition probing levels of $\Pi^+$ symmetry are observed as narrow resonances limited by the Doppler width at 100 K. Line positions for these transitions are determined to an estimated absolute accuracy of 0.06 cm$^{-1}$. Predissociation line widths of $\Pi^+$ levels are extracted from the absorption spectra. A comparison with the recent results on a study of the $D^1\Pi_u$ state in H$_2$ and D$_2$ reveals that the predissociation widths scale as $\mu^{-2}J(J+1)$, with $\mu$ being the reduced mass of the molecule and $J$ the rotational angular momentum quantum number, as expected from an interaction with the $B^1\Sigma_u^+$ continuum causing the predissociation.

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the early years of quantum mechanics the hydrogen molecule has been studied and has provided theorist with an ideal testing ground for calculations. The stable isotopic variants of H$_2$, namely D$_2$ and HD, allow for testing mass scaling effects. The $D^1\Pi_u$ state was found to undergo predissociation above the third vibrational level (the fourth vibrational level for D$_2$ and HD) which can be accurately described by Fano’s theory of a single bound state interacting with a continuum (Fano 1961).

The $D^1\Pi_u$ state of HD has received considerably less interest compared to the other two stable isotopic variants. On the experimental side Takezawa and Tanaka (1972) determined $Q(1)$ transitions for the lowest three vibrations accurate to within a few cm$^{-1}$. Monfils (1965) measured level energies for both $\Pi^+$ and $\Pi^-$ parity components up to $v' = 8$ with accuracies of $\sim 5$ cm$^{-1}$. A profile analysis of the predissociated line shapes was conducted by Dehmer and Chupka for $v' = 7$ and 9 as well as a separate study focusing on the line positions for the $R(0)$, $R(1)$ and $Q(1)$ transitions from $v' = 7$–16 (Dehmer and Chupka 1980, 1983) with accuracies of $\sim 4$ cm$^{-1}$. Theoretically, Kolos and Rychlewski (1976) have calculated the vibrational levels up to the $n = 3$ dissociation limit for the $D^1\Pi_u$ state, while Abgrall and Roueff (2006) calculated term values for the lowest three vibrations ($v' = 0–2$) in a study focusing mainly on the Lyman and Werner bands of HD.

This work on HD is an extension to the studies of the $D^1\Pi_u$ state in H$_2$ and D$_2$ (Dickenson et al 2010, 2011). The measurements were obtained with the vacuum ultraviolet (VUV) Fourier transform spectrometer (FTS) at the DESIRS beamline of the synchrotron SOLEIL. The line widths of transitions probing $\Pi^+$ levels for all three hydrogen isotopomers are used to verify scaling laws for the predissociation in the $D^1\Pi_u$ state.
Other prominent spectral features are associated with the resonances that appear in the spectrum. Bet al. samples of data over the optical path difference, resulting in an outside of the T-shaped cell. A study of the Lyman and Werner bands of HD (Ivanov 2010) has been used previously in operational from 40 to 200 nm. It has been used previously in the VUV FTS is a scanning wavefront division interferometer of de Oliveira et al. (2010) and is accurate to within 4–5 cm\(^{-1}\) (Sprecher et al 2010) many auto-ionization features present in the gas filter which is used to remove higher order harmonics of the selected wavelength produced by the undulator. The transition is the \((3p)^6(2P_{3/2})9d((3/2)|(3p)_6^1\Sigma_g^+\) at 125 718.13 cm\(^{-1}\) known to an accuracy of 0.03 cm\(^{-1}\) (Sommavilla et al 2002).

3. Theory

The predissociation of the D\(^1\Pi_u\) state is due to a strong Coriolis coupling to the continuum of the B\(^1\Sigma_u^+\) state (Monfils 1961). Due to the \(\Sigma^+\) character of the continuum, transitions probing levels of \(\Pi^-\) symmetry are not affected by this interaction and are only very weakly predissociated due to coupling with the lower lying C\(^1\Pi_u\) continuum (Glass-Maujean et al 2010). A single continuum interacting with a bound state is described by Fano’s theory (Fano 1961) and produces broadened asymmetric absorption profiles described by the Fano function. For more details we refer to our previous works (Dickenson et al 2010, 2011). The widths, broadened by lifetime shortening due to the predissociation are given by

\[
\Gamma_\nu = 2\pi|\langle \psi_B|H(R)|\psi_D_\nu \rangle|^2, \tag{1}
\]

where \(\psi_B\) and \(\psi_D\) are the wavefunctions of the \(B^1\)continuum and the discrete \(D\) state, respectively. Here, the energy level \(B'_\nu\) of the \(B^1\) state is taken equal to the non-perturbed energy of the discrete level \(D_\nu\). The rotational operator, \(H(R)\), is the \(\overrightarrow{T} \cdot \overrightarrow{R}\) operator (also responsible for the \(\Lambda\)-doublet splitting) which causes the predissociation widths of levels \(D_\nu\) to scale as

\[
\Gamma_\nu \propto \frac{1}{\mu^2}J(J + 1), \tag{2}
\]

where \(\mu\) is the reduced mass of the molecule and \(J\) is the rotational quantum number. The reduced mass for the three isotopomers \(H_2\), HD and D\(_2\) are 0.5, 0.67 and 1.0 amu, respectively.

4. Results and discussion

The region above the second dissociation limit in HD is a complex multi-line spectrum that when cooled to liquid nitrogen temperatures consists of six overlapping Rydberg series (Dehmer and Chupka 1983). The absorption spectrum is heavily congested making a complete analysis of all spectral features a challenge. In particular, the D\(^1\Pi_u\) state is recognizable from the broadened Beutler–Fano profiles, aiding the assignment thereof. Our assignments agree with the previous works of Monfils (1965) and Dehmer and Chupka (1983) which are accurate to within 4–5 cm\(^{-1}\). The largest discrepancy occurs for the D\(^1\Pi_u\)(\(v' = 9\))–X\(^1\Sigma_g^+\)(\(v'' = 0\)) band, differing from the present line positions by \(\sim 8\) cm\(^{-1}\) possibly attributable to wavelength drive slippage of the monochromator, as mentioned by the authors. Beyond \(v' = 16\) the identifications are aided by the calculations of the band heads made by Kołos and Rychlewski (1976) accurate to within 1–3 cm\(^{-1}\). From an estimate of the \(\Lambda\)-doublet splitting, the \(Q(1)\) transitions could be identified. The \(R(1)\) transitions beyond \(v' = 15\) were too weak to be observed.

The \(Q\)-branch transitions, observed as narrow resonances limited by Doppler broadening, were observed up to \(v' = 18\).
Table 1. Transition frequencies of $Q$-branch transitions probing levels of $\Pi^-$ symmetry. $\Delta$ represents a comparison with the previous measurements of Monllís (1965) for $\nu' = 0$–6 and Dehmer and Chupka (1983) for $\nu' = 7$–16, defined as the present measurement minus the previous measurements. All values in cm$^{-1}$.

| Transition frequency | $\Delta$ | Transition frequency | $\Delta$ |
|---------------------|---------|---------------------|---------|
| $D-X(0,0)$          |         | $D-X(1,0)$          |         |
| $Q(1)^a$            | 129 675.18 | $Q(1)^a$           | 129 914.07 | 5.10 |
| $Q(2)$              | 129 895.63 | $Q(2)$             | 129 895.63 | 0.07 |
| $Q(3)$              | 129 914.07 | $Q(3)$             | 129 914.07 | 0.07 |

Table 2. Transition frequencies of $R$-branch transitions probing levels of $\Pi^+$ symmetry. $\Delta$ represents a comparison with the previous measurements of Monllís (1965) for $\nu' = 0$–6 and Dehmer and Chupka (1983) for $\nu' = 7$–16 defined as the present measurement minus the previous measurements. $\Gamma$ represents the predissociation width. All values in cm$^{-1}$.

| Transition frequency | $\Gamma$ | Transition frequency | $\Delta$ |
|---------------------|---------|---------------------|---------|
| $D-X(0,0)$          |         | $D-X(1,0)$          |         |
| $R(0)^d$            | 113 666.07 | $R(0)^d$           | 115 005.76 | 1.17 |
| $R(1)^d$            | 113 666.72 | $R(1)^d$           | 115 005.76 | 4.21 |

and are listed in table 1. The $R$-branch transitions which are broadened for $\nu' \geq 4$, were also observed up to $\nu' = 18$ ($R(0)$ transitions only). Transition energies and predissociated widths for these transitions are listed in table 2. All line positions and predissociated widths listed in the tables stem from a deconvolution procedure as described in the previous work on $D_2$ (Dickenson et al. 2011). Briefly, the absorption profiles are first convoluted with a Gaussian function representative of the Doppler profile at 100 K. In the second step, the Beer–Lambert law is included, accounting for the nonlinear absorption depth. Finally, the resulting profiles are convoluted with the instrument function and the fit parameters are then optimized by a standard least-squares fitting routine. Included in the parameters are the points to an unbounded, cubic spline fit of the background. These are optimized along with the line shape parameters resulting in a fit of the background. A sample fit of the $Q(1)$, $R(1)$ and $R(0)$ transitions belonging to the $D-X$ (6,0) band is shown in figure 2. The $Q(1)$ transition has a width of approximately 0.6 cm$^{-1}$ which stems from the contribution of the instrument width of 0.33 cm$^{-1}$ and the Doppler width of 0.5 cm$^{-1}$ and represents the limiting resolution for the particular configuration of the FTS used.

In this analysis of the line widths, the Beutler–Fano asymmetry of the line shape, represented by the Fano $q$-parameter was included by fixing the $q$-values to their theoretical prediction. Upon mass-scaling the $q$-parameters ($q \propto \mu$), it follows that $q \sim -25$ for $R(0)$ and $q \sim -15$ for $R(1)$ transitions in HD (Glass-Maujean 1979, Dickenson et al. 2011). The present data did not permit to perform a reliable two-parameter fit to extract both $q$ and $\Gamma$. This is in part due to the method of recording the spectra in absorption against a fluctuating continuum level. For further discussion, see the previous work on $D_2$ (Dickenson et al. 2011).
4.1. Spectroscopic results

The Q-branch transitions, i.e. transitions probing states of \( \Pi \) symmetry and transitions belonging to bands with \( \nu' \leq 3 \) are not predissociated and observed as narrow features with width, \( \sim 0.6 \text{ cm}^{-1} \), equal to the Doppler width of HD at 100 K convoluted with the instrument width. Uncertainty in the reported line positions in table 1 and for the unpredissociated bands listed in table 2 is estimated at 0.06 cm\(^{-1} \). For slightly saturated lines, blended lines and weak lines the uncertainty estimate increases to 0.08 cm\(^{-1} \).

The R- and P-branch transitions are observed as broadened due to the life-time shortening caused by predissociation. Several small portions of the spectra are displayed in figure 3 including the \( D^1 \Pi_u \) \( (\nu' = 7-9) \)-\( X^1 \Sigma^+ \) bands which display typical predissociated broadening. These transitions were fitted with convoluted profiles and the resultant line positions and widths are listed in table 2. The \( P(2) \) and \( R(2) \) transitions for bands with \( \nu' \geq 3 \) were observed as extremely weak as a result of the fact that most of the rotational population resides in the \( J' = 0 \) and 1 levels. We estimate an uncertainty of 0.20 cm\(^{-1} \) on the line positions of the \( R(0) \) transitions which were observed to be \( \sim 3 \text{ cm}^{-1} \) broad and a 0.4 cm\(^{-1} \) uncertainty estimate on the \( R(1) \) transitions observed at widths of \( \sim 7 \text{ cm}^{-1} \). There were a number of blended lines, most of which could still be fitted. Those lines affected severely by blending are indicated in the table and the estimated line position uncertainty is doubled.

4.2. Predissociated widths

Figure 4 depicts the predissociated widths as a function of the excess energy above the \( n = 2 \) dissociation limit for all three stable isotopomers, H\(_2\), D\(_2\) as determined in previous work (Dickenson et al 2010, 2011) and the newly determined HD widths. The dissociation limits used for H\(_2\), D\(_2\) and HD were H(1/2)\( ^1S_0 \), H(2/2)\( ^1S_0 \), D(1/2)\( ^1D_2 \) and H(1/2)\( ^1S_0 \)+D(2/2)\( ^1D_2 \), respectively (Eyler and Melikechi 1993). The measured widths have been scaled by their respective reduced mass squared and the rotational dependence has been removed by dividing through by \( J(J+1) \). The data for H\(_2\) between 5000 and 8000 cm\(^{-1} \) are missing due to blending with the \( R' \) state in this region. Agreement between the three isotopomers for both \( J' = 1 \) (derived from \( R(0) \) transitions) and \( J' = 2 \) (derived from \( R(1) \) transitions) rotational levels is good yielding further proof of the applicability of the simple two-state model to the predissociation of the \( D^1 \Pi_u \) state in all three stable hydrogen isotopomers. At the present level of accuracy, the data indicate that \( u-g \) symmetry breaking effects in HD do not play a role in the predissociated life-times and that the predissociation can be fully described by the \( |\langle \psi_{Bu} | H(R) | \psi_{Dv} \rangle| \) interaction.

4.3. \( \Lambda \)-doublet

The \( \Lambda \)-doublet splitting, as depicted in figure 5, was determined by adding the ground state level energy to the \( Q \)-branch transitions (Komasa et al 2011) and subtracting this from the \( R \)-branch transitions probing the same \( J' \) but opposite...
The present results on HD and the results of H$_2$ (Dickenson et al. 2010, 2011). If the assumption can be made that the $B'$ state is the sole perturber causing the $\Lambda$-doubling, the $\Lambda$-douplet splitting can be represented as

$$\Lambda_{\nu'}(J') \propto \sum_{\nu,\epsilon} |\langle \psi_{B',\nu}\psi_{D',1}(R)\psi_{D',\epsilon}\rangle|^2 \frac{E_{\Pi^+}}{E_{\Pi^+} - E_{\Pi^+}},$$

(3)

where summation over all $B'$ levels includes the bound levels below $n = 2$ and an integral over the $B'$ continuum. Interaction with the $B'$ levels of $^1\Sigma^+$ symmetry causes the $\Pi^+$ ($e$) levels of the $D^1\Pi_u$ state to shift upwards, while the $\Pi^-$ ($f$) levels are unaffected. Similarly as in the deviation of the predissociation widths, the $\Lambda$-douplet splitting then scales like $\mu^{-2}J(J+1)$. The present results on HD and the results of H$_2$ (Dickenson et al. 2010) perfectly match this scaling, while the $\Lambda$-douplet splittings in D$_2$ (Dickenson et al. 2011) are somewhat too large in this comparison.

5. Conclusion

The VUV FTS observations on the $D^1\Pi_u$ state have been extended to HD. This work represents the highest resolution study on this state performed so far. The predissociated line shapes were analysed resulting in predissociated line widths determined to a high level of accuracy. The present and previous studies show, through the mass scaling and rotational scaling, that the predissociation in the $\Pi^+$ parity states of the $D^1\Pi_u$ state can be modelled by a rotational interaction with the continuum of the $B'^1\Sigma^+_u$ state. In the case of HD, the $u-g$ symmetry breaking does not play a role in the predissociated widths at the present level of accuracy.

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References

Abgrall H and Roueff E 2006 Astron. Astrophys. 445 361

de Oliveira N, Joyeux D, Phalippou D, Rodier J C, Polack F, Vervloet M and Nahon L 2009 Rev. Sci. Instrum. 80 043101

de Oliveira N, Roudjane M, Joyeux D, Phalippou D, Rodier J C and Nahon L 2011 Nature Photon. 5 149

Dehmer P and Chupka W 1980 Chem. Phys. Lett. 70 127

Dehmer P and Chupka W 1983 J. Chem. Phys. 79 1569

Dickenson G D et al 2010 J. Chem. Phys. 133 144317

Dickenson G D et al 2011 Mol. Phys. 109 2693

Eyler E E and Melikechi N 1993 Phys. Rev. A. 48 R18

Fano U 1961 Phys. Rev. 124 1866

Glass-Maujean M 1979 Chem. Phys. Lett. 68 320–3

Glass-Maujean M, Jungen C, Schmoranzer H, Knie A, Haar I, Hentges R, Kietsch W, Jankulski K and Ehresmann A 2010 Phys. Rev. Lett. 104 183002

Ivanov T, Dickenson G, Roudjane M, de Oliveira N, Joyeux D, Nahon L, Tchang-Brillet W-Û and Ubachs W 2010 Mol. Phys. 108 771

Kolos W and Rychlewski J 1976 J. Mol. Spectrosc. 62 109

Komasa J, Piszczatowski K, Lach G, Przybytek M, Zejziorski B and Pachucki K 2011 J. Chem. Theory Comput. 7 3105

Monfils A 1961 Acad. Roy. Belg. Bull. Cl. Sci. 5 599

Monfils A 1965 J. Mol. Spectrosc. 15 265

Sommavilla M, Hollenstein U, Greetham G and Merkt F 2002 J. Phys. B: At. Mol. Opt. Phys. 35 3901

Sprecher D, Liu J, Jungen C, Ubachs W and Merkt F 2010 J. Chem. Phys. 133 111102

Takezawa S and Tanaka Y 1972 J. Chem. Phys. 56 6125