OBSERVATION OF INTER-RYDBERG TRANSITIONS IN H_2 COINCIDING WITH DIFFUSE INTERSTELLAR BANDS

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ABSTRACT

In a laboratory study inter-Rydberg transitions originating from the lowest rotational levels of the $C\ ^1\Pi\ v = 5$ and $v = 6$ states of molecular hydrogen are found to coincide with frequency positions and widths of diffuse interstellar bands. It is the first time that diffuse interstellar bands are assigned to transitions measured in gas-phase molecules that are known to exist in interstellar space.

Subject headings: ISM: molecules — molecular processes — methods: laboratory

The problem of the diffuse interstellar bands (DIBs) has challenged spectroscopists and astrophysicists ever since the first accounts of their observation in the 1930s. By now some 200 unidentified absorption features of various strengths and line shapes throughout the entire visible wavelength range are observed in the line of sight of stars of different types (Jenniskens & Désert 1994; Herbig 1995). Despite extensive laboratory studies, the carriers of the DIBs still have to be identified. Even the debate whether to assign the DIBs to gas-phase molecules or to solid particles has not yet been fully resolved. In recent years the gas-phase hypothesis has become favored, and classes of polycyclic aromatic hydrocarbon (PAH) molecules (Salama et al. 1996) and unsaturated hydrocarbon chain molecules (Fulara et al. 1993) were proposed as DIB carriers. Furthermore, two DIB features at wavelengths in the near-infrared were assigned to the C_{60}^+ ion (Foing & Ehrenfreund 1994). The assignment of the proposed carriers is based on a comparison of DIB positions with laboratory spectroscopic information derived from matrix studies. The evidence is ambiguous because in matrices spectral lines are severely broadened and shifted by unknown amounts from their true gas-phase position. A coincidence between a strong DIB feature and a gas-phase molecule was observed for the chlorin molecule ($C_{20}H_{10}N_4$) (Miles & Sarre 1992), but it is unlikely for this porphyrin molecule to exist in large enough abundance in interstellar space to cause the DIB.

Sorokin & Glownia (1995) proposed a model in which inter-Rydberg transitions in gas-phase molecular hydrogen cause the DIBs. The H_2 hypothesis is appealing because H_2 is known to be omnipresent in interstellar space, in abundances of some 10 orders of magnitude higher than the above-mentioned species. The difficulty with the H_2 hypothesis is to devise a pumping scheme that can explain the population of selected rovibronic levels of electronically excited states of hydrogen involved in DIB absorptions. Sorokin and Glownia proposed such schemes, initially based on resonance-enhanced two-photon excitation (Sorokin & Glownia 1995), and later on near-resonance stimulated Raman pumping induced by stellar vacuum-ultraviolet (VUV) radiation (Sorokin & Glownia 1996). Their work was criticized by Snow (1995).

Models for the DIBs relying on gas-phase molecules as carriers have two key requirements. One is to provide an explanation for the molecular abundances along the lines of sight of observation, involving a chemical, as well as a radiative

transfer model. The second requirement is to establish firm spectroscopic evidence by showing that the DIB features coincide with transitions in gas-phase molecules. Inspired by the work of Sorokin and Glownia, we have employed a XUV-visible double-resonance laser setup to investigate spectroscopic aspects of the H_2 hypothesis. Initially, we focused on recording transitions via the $C\ ^1\Pi\ v = 9$ intermediate state in H_2, first proposed as a DIB-carrying state. Although some coincidences with DIBs were found, the observed spectral features in excitation from $C\ ^1\Pi\ v = 9\ J$ states do not match the DIBs in specific ranges 766–788 nm (Hinnen & Ubachs 1995) and 700–740 nm (Hinnen & Ubachs 1996). Particularly, the observation of many strong resonances in H_2 at wavelengths where no DIBs are documented could be considered as evidence against the H_2 hypothesis. However, the observed spectral patterns and regularities in the spectra resembled DIB features, and this encouraged us to proceed in our search for coincidences between DIBs and strong inter-Rydberg transitions in molecular hydrogen. Particularly, the well-understood concept that transitions to autoionizing and predissociating states in H_2 can account for a wide variety of line shapes, including asymmetries, is stimulating.

During the course of laboratory investigations we found that in excitation from $C\ ^1\Pi$ rovibronic states in the energy range near the ionization potential of H_2, only a single strong resonance exists. In Figures 1 and 2 spectral recordings from $C\ ^1\Pi\ v = 5$ and $v = 6$ intermediate states into this energy range are displayed. Here only a limited energy range is shown, but it is noted that no other strong features are observed in a range spanning 1000 cm^{-1}. At the temperatures prevailing in interstellar clouds, only $J = 0$ (para-hydrogen) and $J = 1$ (ortho-hydrogen) ground states are populated. Via $R(0)$, $R(1)$, and $Q(1)$ transitions, respectively, $C\ ^1\Pi$ $J = 1(-)$, $2(+)$, and $1(+)$ intermediate states are excited. These states for vibrational quantum numbers $v = 5$ and $v = 6$ were used as intermediates and further excited in a XUV-visible double-resonance experiment as described previously (Hinnen & Ubachs 1995). In fact, only two different final states are probed by the six transitions listed in Table 1. For para-hydrogen, probed via $J = 1(-)$, a resonance at 124701.9 cm^{-1} is excited, via either $C\ ^1\Pi\ v = 5$ or $v = 6$. The spectroscopy of the $C\ ^1\Pi$ state was performed in a high-resolution experiment, resulting in energy levels determined with an accuracy of 0.03 cm^{-1} (Reinhold, Hogervorst, & Ubachs 1996).
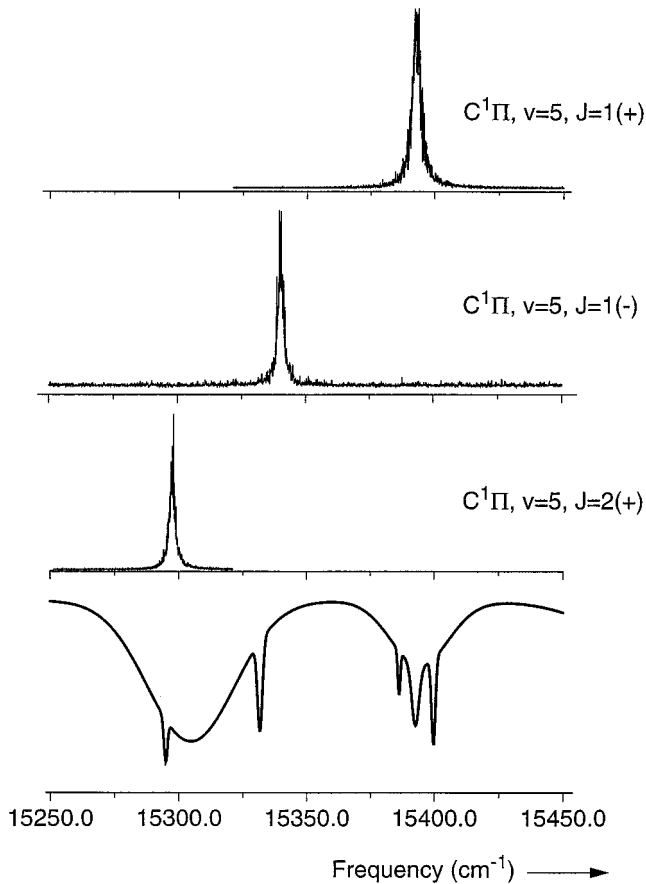
FIG. 1.—Observed double-resonance spectra of H_2 via $C\ ^1\Pi\ v = 5$ intermediate states and in the lower part a reconstructed DIB spectrum from the data of Jenniskens & Désert (1994).
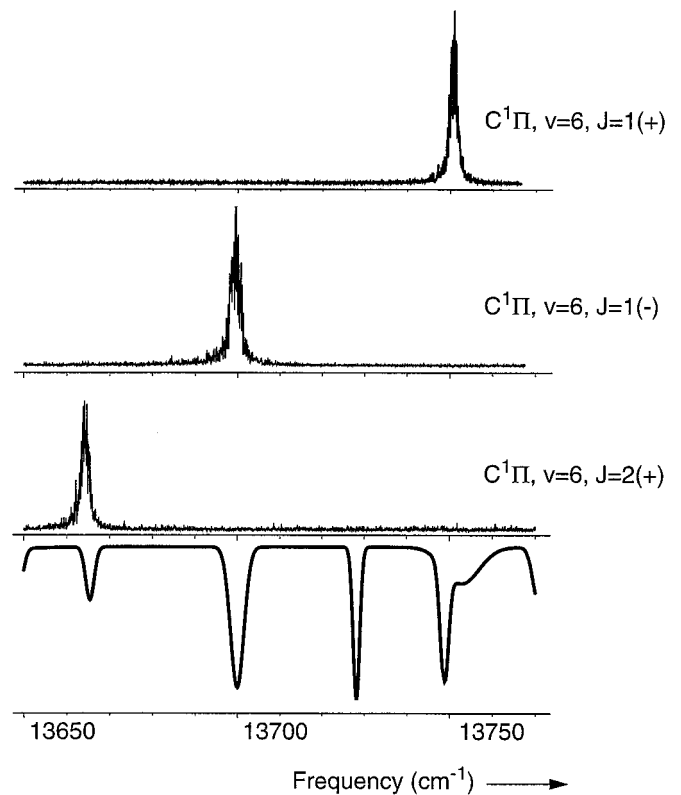

FIG. 2.—Observed double-resonance spectra of H_2 via $C\ ^1\Pi\ v = 6$ intermediate states and in the lower part a reconstructed DIB spectrum from the data of Jenniskens & Désert (1994).

For ortho-hydrogen, routes are available via $J = 1(+)$ and $2(+)$ and via $C\ ^1\Pi\ v = 5$ and $v = 6$, probing the same final state at 124752.5 cm^{-1}. This resonance is just below the $X\ ^2\Sigma_g^+ v^+ = 0\ N^+ = 3$ ionization limit, and by close inspection a Rydberg progression can be discerned on the low-energy flank of the resonance. The character of this autoionizing state is unknown, apart from the conclusion that it has to be a $J = 1(-)$ or $J = 2(-)$ state of gerade symmetry. Frequency positions are obtained by interpolation between optogalvanically detected Ar lines, resulting in a 0.3 cm^{-1} accuracy. Since the experimental resolution is 0.1 cm^{-1}, the widths of order 2 cm^{-1} (in purely Lorentzian line shapes) present evidence of diffuseness of the observed features, which is due to autoionization and predissociation of the final states.

In Figures 1 and 2 a reconstructed DIB spectrum is shown as well, based on the frequency positions and widths obtained in a recent high-resolution DIB survey by Jenniskens & Désert (1994), while in Table 1 a numerical comparison is made between observed resonances in H_2 and positions and widths of DIBs as listed there. For convenience of use values are also listed in Å in air. Throughout this paper we use an index of refraction of $n = 1.000276$, as in Jenniskens & Désert (1994). Three H_2 resonances, starting from $C\ ^1\Pi\ v = 5\ J = 1(+)$, $C\ ^1\Pi\ v = 6\ J = 1(-)$, and $C\ ^1\Pi\ v = 6\ J = 2(+)$, match the frequency of listed DIBs within given error limits. The lines originating from $C\ ^1\Pi\ v = 5\ J = 2(+)$ and $C\ ^1\Pi\ v = 6$ $J = 1(+)$ are close to specified DIB positions but fall outside the error margins. A sixth resonance, recorded from $C\ ^1\Pi$ $v = 5\ J = 1(-)$, is separated from a DIB position by some 10 cm^{-1}.

The line widths in the present study are derived by fitting the experimental profiles to a Lorentzian. Jenniskens & Désert (1994) determined DIB widths in terms of area-to-height ratios, assuming a Gaussian line shape. So for comparison with a Lorentzian, a conversion factor of $(\pi \log 2)^{1/2} \approx 1.47$ has been incorporated. The presently observed widths, falling in the range 1.5–3 cm^{-1} with some scatter, coincide in most cases with the widths of the DIB features.

It is of interest to compare our findings with the model and predictions of Sorokin & Glownia (1996). In their pump model based on Raman lasing, strong enhancement of transitions involving the $J = 1(-)$ and $J = 2(+)$ intermediate states in $C\ ^1\Pi$, which are both of (e)-symmetry, is predicted. In an alternative pump scheme, simultaneous two-photon excitations play a role, in which case excitations via Q lines, thus $J = 1(+)$ states, would be favored since Q lines are strongest in a $^1\Pi_u$–$^1\Sigma_g^+$ transition. Sorokin & Glownia (1996) relate more than 70 DIBs to transitions in molecular hydrogen. Most of their assignments involve transitions to excited states of $^1\Sigma_g^+$ symmetry. In fact, the DIB at 15332 cm^{-1} (6520.7 Å) is assigned to an $R(2)$ transition in the $EF\ ^1\Sigma_g^+$–$B\ ^1\Sigma_u^+$ (13, 2) band, as well as to the $R(2)$ line of the $O\ ^1\Sigma_g^+$–$B\ ^1\Sigma_u^+$ (0, 11) band. Similarly the 15392 cm^{-1} (6494.9 Å) DIB is assigned to the $Q(2)$ line of the $EF\ ^1\Sigma_g^+$–$C\ ^1\Pi_u$ (28, 1) band, while the 13655 cm^{-1} (7321.1 Å) DIB is assigned to the $Q(2)$ line of the $P\ ^1\Sigma_g^+$–$C\ ^1\Pi_u$ (0, 2) band. The $EF\ ^1\Sigma_g^+$ state and the lowest vibrational states of $O\ ^1\Sigma_g^+$ and $P\ ^1\Sigma_g^+$ are below the ionization

TABLE 1

OBSERVED TRANSITIONS FROM $C\ ^1\Pi\ v = 5$ AND $v = 6$ INTERMEDIATE STATES IN H$_2$ AND COMPARISON WITH DIFFUSE INTERSTELLAR BANDS

Intermediate State	Observed (cm^{-1})	γ_{obs} (cm^{-1})	Observed (Å air)	DIB Position (cm^{-1})	Γ_{DIB} (cm^{-1})
$C\ ^1\Pi, v = 5, J = 1(+)$	15392.5 (0.3)	2.8 (0.3)	6494.9 (0.1)	15392.4 (0.6)	2.2 (0.8)
$J = 2(+)$	15297.6 (0.3)	2.7 (0.3)	6535.0 (0.1)	15294.6 (0.3)	1.1 (0.1)
$J = 1(-)$	15340.2 (0.3)	3.1 (0.3)	6517.0 (0.1)	15331.5 (0.6)	1.6 (0.6)
$C\ ^1\Pi, v = 6, J = 1(+)$	13740.6 (0.3)	1.8 (0.3)	7275.7 (0.2)	13738.7 (0.2)	1.4 (0.2)
$J = 2(+)$	13654.2 (0.3)	2.1 (0.3)	7321.7 (0.2)	13655.4 (1.2)	1.6 (0.4)
$J = 1(-)$	13689.4 (0.3)	2.4 (0.3)	7302.9 (0.2)	13689.7 (0.6)	2.6 (0.6)

NOTE.—Positions and widths of DIBs are given by Jenniskens & Désert 1994. Γ_{obs} denotes widths (FWHM) of observed transitions; values for Γ_{DIB} were corrected as explained in the text.

potential of hydrogen and also below the H($n = 1$) + H($n = 2$) dissociation limit. Therefore these states have long lifetimes, do not predissociate nor autoionize, and were indeed observed in emission in the spectra of Dieke (Crosswhite 1972). Many of the assignments of so-called sharp DIBs by Sorokin & Glownia (1996), including the ones mentioned above, involve long-lived $^1\Sigma_g^+$ upper states in H$_2$. The fact that even the sharp DIBs are truly diffuse (i.e., broader than expected for a bound-bound transition in an atomic or molecular system) is not accounted for. It is conceivable that the assignment of DIB features within the framework of nonlinear optical schemes may explain some diffuseness. In the present work some "sharp DIBs" are assigned to transitions to autoionizing states in hydrogen, in contrast to the suggestions of Sorokin & Glownia (1996). Such an assignment succeeds in explaining the diffuseness of the DIBs.

In their paper Sorokin & Glownia (1996) assign the broad and strong $\lambda4429$ DIB to the combined effect of photoionizing transitions originating in the $C\ ^1\Pi\ v = 1\text{–}5\ J = 1(-)$ and $J = 2(+)$ intermediate states. This hypothesis was tested in our investigations by preparing each of these quantum states individually and then scanning a second laser around 443 nm. In all cases (we were restricted to $v = 2\text{–}5$) a dense spectrum consisting of many narrow and broad peaks was observed, without the occurrence of a particularly strong feature coinciding with the $\lambda4429$ DIB. One example is shown in Figure 3.

The present work, dealing with only a few of the weaker out of the 200 observed DIBs, can be considered an *Ansatz* for

FIG. 3.—Observed double-resonance spectra of H$_2$ via the $C\ ^1\Pi\ v = 3$ $J = 2(+)$ intermediate state with a second laser tuned in the wavelength range of the strong $\lambda4429$ DIB, showing that such an excitation scheme does not explain the DIB feature. Similarly, spectra of $J = 2(+)$ and $J = 1(-)$ states of $C\ ^1\Pi\ v = 2\text{–}5$ were recorded, yielding the same conclusion.

future work. Although our previous reports on XUV-visible double-resonance studies in H$_2$ (Hinnen & Ubachs 1995, 1996) merely produced negative results for possible coincidences, the present report assigns tentatively several inter-Rydberg transitions in H$_2$ to DIBs. Three transition frequencies match the DIBs within error margins. Two more resonances, observed in excitation from $C\ ^1\Pi\ v = 5\ J = 2(+)$ and $C\ ^1\Pi\ v = 6$ $J = 1(+)$ are in a strict sense not coincident with listed DIBs. These DIBs are weak and superposed on the flank of a broad structure (see Figs. 1 and 2) from which positions are determined in a deconvolution procedure. In view of this and the fact that these two DIBs are nevertheless found to overlap with the observed H$_2$ resonances within the width of the line profile, the latter two resonances may be considered as possible coincidences. Future DIB searches, with an increased resolution of an order of magnitude demonstrated by Sarre et al. (1995), may settle this issue. The sixth resonance does not even nearly coincide with a known DIB feature. The fact that a DIB exists at 10 cm^{-1} distance may be classified as pure chance.

Important additional evidence is the observation that only a single strong resonance is excited from each intermediate state in a wide wavelength range. We hope that these results will stimulate further investigations into the modeling of H$_2$ excitations under the influence of strong VUV-radiation fields, along the lines of the work of Sorokin and Glownia. Also, a stimulus for future DIB searches may be derived from our results. The strong autoionizing resonances can also be probed via $C\ ^1\Pi$ $v = 4$ and $v = 7$ intermediate states. At these frequencies, predicted at 17071.0 cm^{-1} ($\lambda_{air} = 5856.3$ Å), 17121.0 cm^{-1} (5839.2 Å), and 17173.8 cm^{-1} (5821.2 Å) for $C\ ^1\Pi\ v = 4$ and at 12150.7 cm^{-1} (8227.7 Å), 12171.9 cm^{-1} (8213.4 Å), and 12221.5 cm^{-1} (8180.0 Å) for $C\ ^1\Pi\ v = 7$, no DIBs are reported yet, but they could be a starting point for future DIB searches. Certainly this range has been searched by Jenniskens & Désert at a high, but limited, sensitivity. The fact that the presently observed H$_2$ resonances coincide with weak DIBs calls for DIB searches at even higher sensitivities, as in the work of Krelowski, Sneden, & Hiltgen (1995), in which features at the predicted wavelengths may or may not be found. The same line of reasoning also holds for the 6517.0 Å resonance in H$_2$.

In conclusion, we report observation of coincidences of inter-Rydberg transitions in molecular hydrogen with weak DIBs. The present assignment of coincidences is to be considered as tentative since the DIB features were reported only in the work of Jenniskens & Désert (1994) and require further confirmation from high-resolution observations. We have lim-
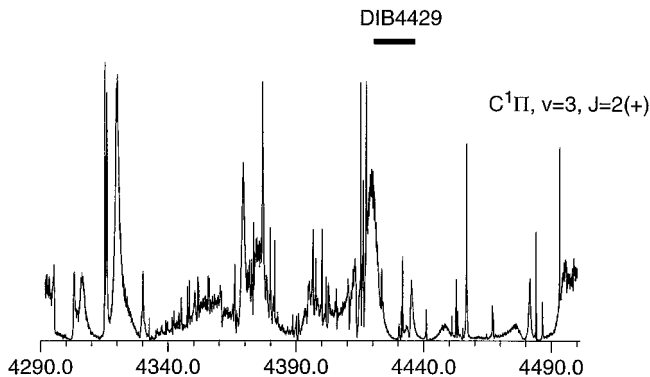
ited ourselves in this work to the spectroscopic aspect of the H_2 hypothesis. For a definite, trustworthy identification of H_2 as a carrier of DIBs, the transitions have to be incorporated in astrophysical models, explaining population densities and absorption strengths of the transitions, based on the chemistry and the radiation fields in the interstellar medium.

Note added in manuscript (*1996 December 5*).—Recently a highly sensitive high-resolution DIB search was performed by Jenniskens et al. (1996) in the wavelength interval 5837–5860

Å. A very weak DIB was found at 5856.5 Å, within the line profile of the predicted line originating in the $C\ ^1\Pi\ v = 4$ $J = 2(+)$ level. No coincidence was found for the predicted line from the $C\ ^1\Pi\ v = 4\ J = 1(-)$ intermediate state.

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