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Further tests concerning the hypothesis of H_2 as the carrier of diffuse interstellar bands

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Abstract

A laboratory search for coincidences of transitions between excited states in H_2 with frequencies of diffuse interstellar bands (DIBs) was performed employing an XUV–Vis laser-based double-resonance scheme. Single quantum levels of various rovibrational states of the C $^1\Pi_u$ state of H_2, populated by means of transitions at 86 nm, were used as intermediate states for the absorption of a visible photon. Although some coincidences are found, a recent hypothesis involving detailed assignments of DIBs to specific transitions in H_2 is not confirmed. Spectral profiles are recorded that mimic characteristic triplet structures and asymmetric lineshapes as observed in DIBs. Based on the present findings the hypothesis of H_2 as the carrier of diffuse interstellar bands is discussed from a more general perspective.

1. Introduction

For as long as six decades diffuse interstellar bands (DIBs) have puzzled astrophysicists, and the problem of their origin is considered to be the longest standing in the history of spectroscopy. These unidentified diffuse absorptions, observed in the spectra of many stars in our galaxy, have attracted increased attention in the past few years [1] and have been attributed to a variety of absorbers, ranging from solid-state particles (grains) to various classes of gas phase molecules [2]. On the basis of spectroscopic arguments (ionic) polycyclic aromatic hydrocarbons (PAHs) such as the naphthalene ion ($C_{10}H_8^+$) [3] and the pyrene cation $C_{14}H_{10}^+$ [4], as well as a class of highly unsaturated hydrocarbons C_nH (with $n = 6, 8, 10$) [5], and the C_{60}^+ ion [6] were proposed as carriers. Consensus now seems to have emerged in identifying such carbon-based gas phase molecules as the most plausible carriers of DIBs. Transitions in these molecules from the ground state to the various excited electronic levels would then give rise to DIB phenomena. Laboratory spectra of these molecules are usually recorded in solid-state matrices at low temperatures, giving rise to broadening effects and unknown frequency shifts with respect to transitions in the gas phase. The hypothesis of carbon-containing molecules as the carrier of DIBs therefore awaits confirmation by laboratory gas phase spectroscopy.

Recently, an alternative carrier was put forward by Sorokin and Glownia [7]. A subset of excited singlet states in molecular hydrogen are proposed to be the absorber states for the DIB-producing phenomena, instead of a class of different molecules. In view of the high abundance of H_2 in the interstellar medium, a model involving H_2 as the carrier of

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DIBs is appealing. An astrophysical mechanism to explain the required column density of excited H_2 was also described by Sorokin and Glownia. In short, a resonantly enhanced two-photon process, involving a Lyman-α (L_α) photon and a visible photon corresponding to the DIB frequency, was proposed to occur. The DIB spectrum in the range 7660–7880 Å was assigned as belonging to absorption features starting in the C $^1\Pi_u^e$ $v=9$, $J=1$–4 excited states in H_2, sufficiently pumped from the $X^1\Sigma_g^+$, $v=11$ state, by L_α radiation. The assignment of specific DIBs to transitions in H_2 was mainly based on well known combination frequency differences of rotational levels in the C $^1\Pi_u^e$ $v=9$ state. The same frequency differences were also found in the DIB spectrum. In a laboratory experiment the specific hypothesis involving the C $^1\Pi_u^e$ $v=9$ state as carrier state for DIBs in the range 7660–7880 Å was shown to be incorrect [8]. Snow [9] commented that insufficient population was to be expected in the C $^1\Pi_u^e$ $v=9$, $J=1$–4 levels to produce the DIBs, specifically due to lower L_α flux than calculated by Sorokin and Glownia. Sorokin and Glownia [10] subsequently proposed a modified model where sufficient population in the various excited states is obtained by stellar VUV-blackbody radiation, enhanced by a Raman-lasing scheme involving again L_α photons. Excited states of H_2, which are coupled to high vibrational levels in the electronic ground state via L_α radiation, are effectively lifetime-enhanced as Raman lasing occurs between these states. This astrophysical model again provides a selective element to identify specific excited states of H_2 as absorber states for the DIBs, without the need of an excessive L_α flux. Based on this model and using known combination differences in excited H_2, Sorokin and Glownia [10] assigned 30 DIBs in the wavelength region 7000–7400 Å to transitions in H_2 between excited states, with the C $^1\Pi_u^{e/f}$ $v=9$, $J=1$–4 levels as absorber states.

The present laboratory experiment tests this assignment of DIBs. Some coincidences between Rydberg–Rydberg transitions in H_2 and DIB frequencies are indeed observed. However, the assignment of the C $^1\Pi_u$ $v=9$ state of H_2 as the carrier of virtually all DIBs in the range 7000–7400 Å could not be confirmed. Based on our findings we will discuss arguments in favour and against the hypothesis of H_2 as the carrier of the diffuse interstellar bands.

2. Experimental observations

Single rotational levels of the C $^1\Pi_u$ $v=9$ Rydberg states of H_2 were selectively prepared by means of tunable narrow-band XUV laser light in an apparatus previously described [11,12]. A beam of coherent XUV radiation perpendicularly intersects a pulse H_2 molecular beam and excites H_2 molecules to the C $^1\Pi_u$ Rydberg state. A second counter-propagating dye laser beam, spatially and temporally overlapping the XUV laser light, excites H_2 further into resonances above the ionization potential. Polarizations of the XUV and visible laser are linear and parallel. As the density of the H_2 molecules in the interaction region is as low as 10^{-5} Torr, and only a fraction is excited into short-lived (≈ 1 ns) intermediate C states, direct absorption measurements are not feasible. Therefore, the technique of (1 XUV + 1 Vis) photoionization and detection of H_2^+ ions is used to record the spectra of transitions in H_2 between excited states. In view of the low densities and the short lifetimes collisional redistribution of the population is excluded.

The XUV beam is generated as an harmonic (3rd) of an intense UV beam. In a previous investigation [8], a strong ion-background signal was found as a result of (1 XUV + 1 UV) photoionization. In the present study the XUV was separated from the UV by means of a special method of localised phase matching [13] in the harmonic conversion process, allowing for background-free ionization signals from the second laser. The wavelength of the visible laser (bandwidth ≈ 0.1 cm^{-1}) was calibrated against simultaneously recorded calibrated lines of uranium [14] and argon [15] by means of optogalvanic detection in a hollow-cathode discharge. The resulting accuracy for the narrow features is 0.2 cm^{-1}.

Several recordings, using different rotational levels of the C $^1\Pi_u$, $v=9$ state as intermediate levels, while scanning the wavelength of the second laser from 7000 to 7400 Å, are displayed in Fig. 1. The spectra show a large number of pronounced resonances, varying in width, strength and line profile. In

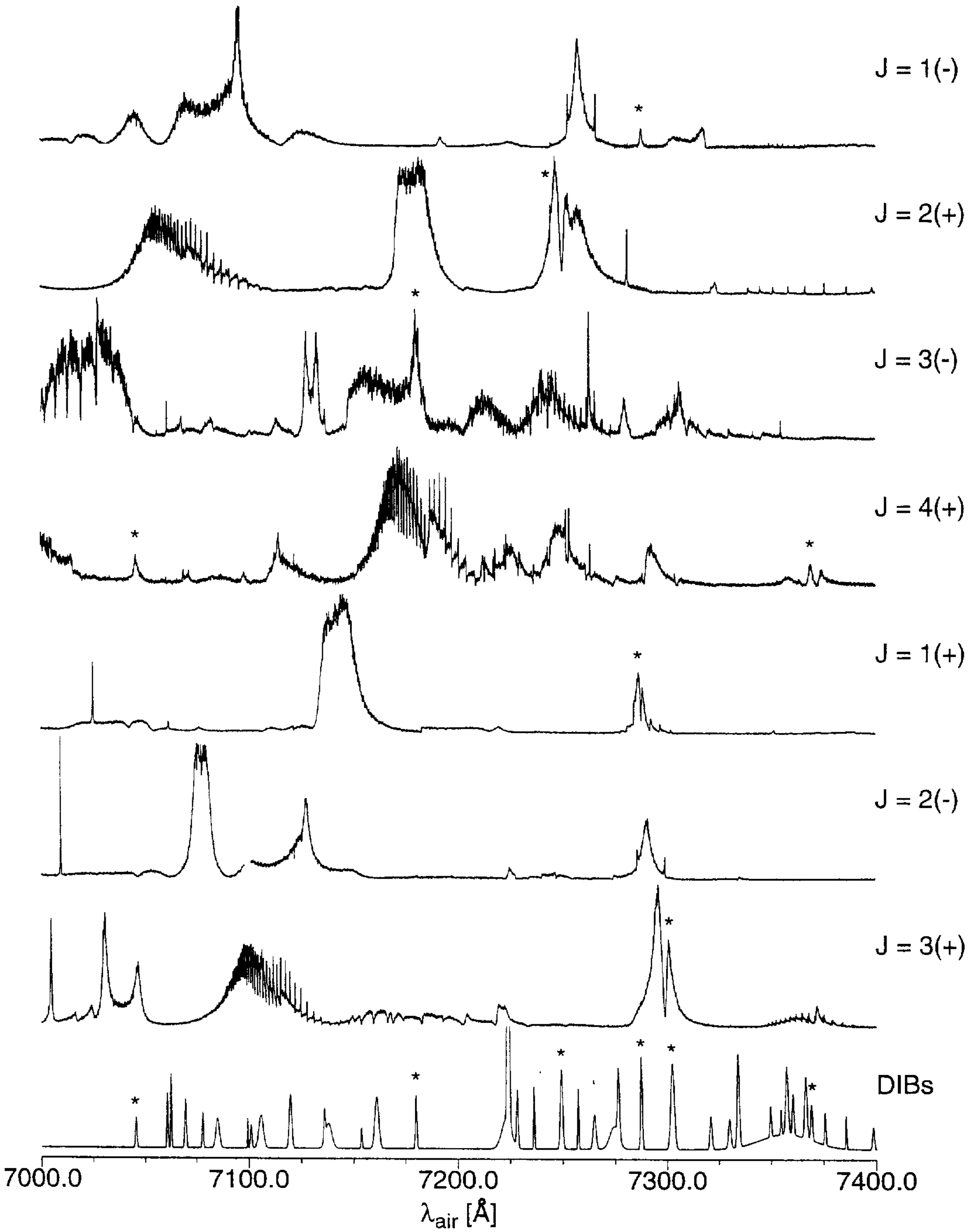

Fig. 1. Spectra recorded via XUV–Vis double-resonance excitation of H_2, with the XUV laser set at the various C $^1\Pi_u$ $v = 9$ J states. The plus (+) and minus (−) signs refer to the total parity of the intermediate state. The spectra are obtained by registration of H_2^+ ion signal, with the visible laser scanned over the wavelength range specified on the horizontal axis. The lower trace shows a reconstructed diffuse interstellar band spectrum in the same wavelength region, using data from Jenniskens and Désert [18]. The wavelength λ is given in Å, in air. Coincidences between observed transitions and DIBs, as specified also in Table 1, are marked with (*).

various cases a Rydberg series can be discerned, which converge to X $^2\Sigma_g^+$, $v^+ = 2$, N limits of the H_2^+ ion. Since the intermediate state is of *ungerade* symmetry, the observed spectral features pertain to autoionizing states of *gerade* symmetry. Selection rules predict that states of $^1\Sigma_g^+$, $^1\Sigma_g^-$, $^1\Pi_g$ and $^1\Delta_g$ electronic symmetry can be excited. Because of angular momentum selection rules each spectrum in Fig. 1 consists of three contributions corresponding to $J' = J$ or $J' = J \pm 1$, with J' (J) the angular momentum of the highly excited (intermediate) state. While the structure of the ungerade Rydberg states in the energy range above the ionization potential is well documented, in experiments as well as in calculations [16], details of the gerade states in this energy region are largely unknown. Future analysis may reveal the nature of couplings between Rydberg series converging to various v^+ limits of H_2^+ and doubly excited states predicted in this energy range [17], but in the present analysis we restrict ourselves to a relation with the diffuse interstellar bands.

A reconstructed DIB spectrum is shown in the lower trace of Fig. 1. This reconstruction is based on a list of line positions and widths for the DIBs [18]; the spectrum is generated by convoluting Gaussian curves, thus masking asymmetries found in DIB observations. Coincidences of two-photon resonances with DIB frequencies are marked with an asterisk. Nevertheless, the observed laboratory spectra do not reproduce the DIB spectrum in the range 7000–7400 Å. In Table 1 a shortlist of coincidences between the observed transitions between excited states in H_2 and DIB frequencies is given.

3. Discussion of experimental results

In the present work laboratory spectra of transitions between excited states in H_2 are compared with diffuse interstellar band frequencies, testing the hypothesis of excited H_2 as a carrier of DIBs. In an XUV–Vis double-resonance experiment, with C $^1\Pi_u^{e/f}$, $v = 9$, $J = 1$–4 levels as intermediate states, several pronounced structures, varying in width, strength and spectral shape are observed. Seven coincidences with DIB frequencies are found. The coincidences, as listed in Table 1, seem accidental and cannot provide proof for the H_2 hypothesis, particularly since the majority of the observed features do not coincide with DIBs in the range from 7000 to 7400 Å. We note that in the present laboratory study the detection technique is biased towards probing H_2^+ ions. Only the autoionization decay channel of the doubly excited singlet gerade Rydberg states is monitored. As was shown in a study on the singlet ungerade Rydberg states of H_2 [16], some doubly excited states completely dissociate, while oscillator strengths for transitions to such states are exceptionally high. There remains the possibility that the DIB phenomena could relate to transitions resulting in photodissociation. However, judging from the ungerade spectrum, it is not likely that the absorption spectra originating in Rydberg states of H_2 are so strongly dominated by the photodissociation channel that the contribution of the presently observed photionization channels is negligible. Attempts to probe the photodissociation decay channel and therewith further test the H_2 hypothesis are in preparation in

Table 1
Coincidences of wavelengths λ_{obs} of observed transitions between excited states of H_2 with diffuse interstellar band wavelengths λ_{DIB} according to the data of Ref. [18]. All wavelengths are given in Å, in air. The first column describes the state, acting as a ground state for the observed resonances, from which a coincidence with a DIB frequency is found. In column 3 resp. 5 the width of the DIB and the width of the observed resonance in H_2 is given. These coincidences are marked with (*) in Fig. 1

Absorber state	λ_{DIB} (Å)	Γ_{DIB} (Å)	λ_{obs} (Å)	Γ_{obs} (Å)
C $^1\Pi_u$, $v = 9$, $J = 1(+)$	7287.6(3)	0.98(30)	7286.6(4)	3.1 [a]
C $^1\Pi_u$, $v = 9$, $J = 1(-)$	7287.6(3)	0.98(30)	7287.8(1)	1.0
C $^1\Pi_u$, $v = 9$, $J = 2(+)$	7249.3(3)	1.34(40)	7246.9(6)	4.5 [a]
C $^1\Pi_u$, $v = 9$, $J = 3(+)$	7302.7(3)	1.99(50)	7301.1(4)	3.1 [a]
C $^1\Pi_u$, $v = 9$, $J = 3(-)$	7180.0(5)	0.88(21)	7180.8(2)	2.5
C $^1\Pi_u$, $v = 9$, $J = 4(+)$	7045.6(3)	0.84(2)	7046.1(2)	1.8
	7369.3(5)	1.04(8)	7369.3(2)	2.0

[a] Asymmetric lineshape observed in the double-resonance experiment.

our laboratory. The conclusion is that the specific C $^1\Pi_u$, $v = 9$ Rydberg state of H_2 can be ruled out as DIB carrier, at least for DIBs in the wavelength range 7000–7400 Å.

The presently applied experimental techniques and

In a recent Letter Snow [9] has commented on the H_2 hypothesis of Sorokin and Glownia. From our perspective we wish to add some arguments in favor as well as against a hypothesis involving excited states of H_2 as carriers of DIBs. Before doing so we below the ionization limit (91.2 nm) of atomic hydrogen is required. DIB intensities are known to be correlated with the density of atomic hydrogen n(H); consequently, a reduced VUV flux below 91.2 nm is present in H-containing interstellar clouds. This reduces the pumping rate of excited levels of H_2 in the diffuse interstellar medium, placing possible constraints on the proposed VUV-blackbody radiation pumping scheme to excite levels in H_2 above this frequency cut-off.

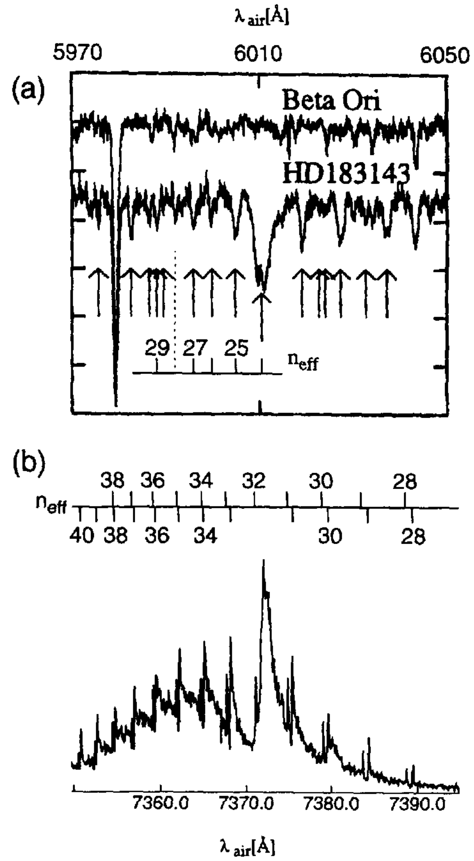

Fig. 2. Comparison of observed weak diffuse interstellar bands in a high-resolution DIB spectrum taken by Krelowski et al. [19] (a) with a measured Rydberg series in H_2 (b). Effective quantum numbers n_{eff} are given for the two observed series in H_2, both converging to the X $^2\Sigma_g^+$, $v^+ = 2$, $N^+ = 3$ limit. Note the similarity of both spectra: a Rydberg-like sequence of lines interrupted by an intense broader feature. A hypothetical Rydberg sequence in the DIB spectrum of a series converging to a limit at 5940.1 Å is shown in the upper trace. The wavelength scales of both spectra are different, and are given in Å, in air.

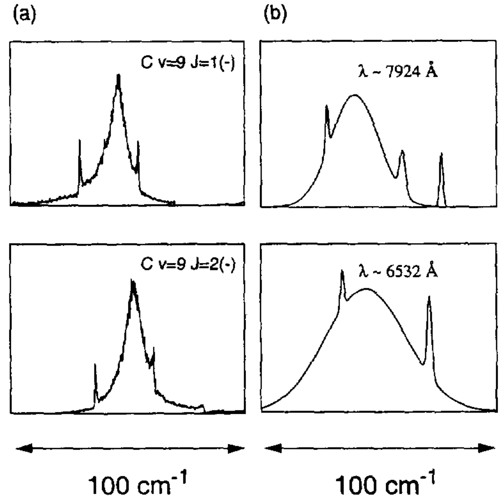

Fig. 3. (a) Observed triplet structures in the laboratory spectra of transitions between excited states in H_2 and (b) resembling spectral outlines as observed in the diffuse interstellar band spectrum [18].

In H_2 Rydberg–Rydberg transitions are also expected in the UV, since autoionizing levels higher up in the ionization continuum can also be probed by UV excitation through intermediate H_2 states, including the C $^1\Pi_u$ $v = 9$ state. Hence there appears to be a *UV problem* connected with the H_2 hypothesis. Despite extensive searches, absorption features in the ultraviolet part of the spectrum that can be assigned to DIBs are not known. However, due to the increasing complexity of stellar spectra towards shorter wavelengths, it is difficult to observe diffuse and shallow absorption features [2]. It is interesting to note in this respect that Tripp et al. [20] have observed an unknown diffuse absorption in the VUV at $\lambda = 1369.13$ Å.

A few yet unidentified *emission* bands were observed in the Red Rectangle nebula [21], with wavelengths converging to those of rather narrow diffuse interstellar bands (i.e. $\lambda_{DIB} = 5797$, 5850 and 6614 Å). If DIBs indeed relate to transitions to autoionizing resonances, emission at these DIB frequencies is not very likely as it is highly improbable that reverse dielectric recombination (i.e. $H_2^+ + e^- \rightarrow H_2^*$) would occur specifically at these wavelengths. However, Sorokin and Glownia [10] have also proposed assignments for a number of DIBs to coincide with bound–bound transitions (i.e. involving fluorescing states) in H_2. These assignments are not tested in the present experiment. Two of the three observed emission bands by Sarre et al. [21] were assigned to such bound–bound transitions [10]; if these assignments were to be correct, the observation of DIBs in emission does not contradict the H_2 hypothesis.

4.2. Arguments supporting the H_2 hypothesis

The timescales of radiative transfer processes in the interstellar medium allow for the population of a fraction of H_2 in electronically excited states. The lifetime of the C $^1\Pi_u$ $v = 9$ and other Rydberg states is only 10^{-9} s, but may be enhanced to 10^{-7} s by the Raman-lasing process proposed by Sorokin and Glownia [10]. Moreover, high vibrational levels of the X $^1\Sigma_g^+$ state of H_2 act as a population trap: the lifetime of these excited vibrational levels of the ground electronic configuration is $\approx 10^5$ s [22], sufficiently long to pick up an L_α photon.

In the literature on DIB phenomena, observed DIB absorption profiles are compared with predicted profiles, in order to find an explanation for the diffusiveness of the features. Cossart-Magos and Leach [23] calculated rotational band envelopes for various polyatomic molecules at different temperatures to find similarities. Alternatively, Shapiro and Holcomb [24] have discussed asymmetric features from the perspective of absorption by impurites in grains. In the present study a wide variety of asymmetric profiles, Fano lineshapes and window resonances, are observed. Although no attempts have been made yet to model such phenomena for excitation of gerade Rydberg states of H_2, the occurrence of such phenomena is generally well understood in the autoionization of two-electron systems. Thus a model involving autoionizing states in H_2 would naturally account for all possible lineshapes.

Shapes and spectral outlines are sometimes used as observational discriminants for the origin of diffuse bands [25]. In the recorded spectra of transitions in H_2 between excited states some characteristic triplet structures are found at various wavelength positions. The observed spectral structures in H_2 have a remarkable topological resemblance with observed DIB profiles, although these are found at different wavelength positions. Two examples of such triplet structures as observed in transitions between excited states in H_2 and two resembling DIB structures are shown in Fig. 2. A similar structure was also found at $\lambda = 7715$ Å, while probing the C $^1\Pi_u$, $v = 9$, $J = 2(-)$ intermediate state [8]. In the DIB spectra other examples, albeit somewhat broader than in Fig. 2, are found at $\lambda = 6935$ and 6050 Å. Possibly such comparisons of spectral structures can guide the way to locating specific intermediate states in H_2 that may act as DIB carriers.

Proposals for carriers of DIBs must be considered from the perspective of column densities as observed or estimated in the interstellar medium, and here the H_2 hypothesis renders its appeal. Herbig [26] has argued that a column density of DIB carriers of the order of $10^{11}/f$ cm^{-2} is needed to produce the observed DIBs, where f is the oscillator strength. The total column density of H_2 towards the O type star ζ Ophiuchi, a reddened star often used for the registration of DIBs, is of the order of 10^{21} cm^{-2} [26]. Rydberg–Rydberg transitions are known to have almost unit oscillator strength ($f \approx 1$) [27], implying that a fraction as small as 10^{-10} of all H_2 molecules in an excited state would be sufficient to produce the DIBs.

5. Conclusion

In the present study we have shown in a laboratory experiment that a recent assignment of 30 DIBs in the wavelength range 7000–7400 Å to transitions from C $^1\Pi_u$, $v = 9$, J states in H_2 is not likely to be correct. Observed spectral lineshapes and regularities in the spectra are compared with spectral outlines of DIB absorptions and resemblances are found. This result may be considered as circumstantial evidence in favor of the H_2 hypothesis. However, the mystery of the origin of diffuse interstellar bands remains unsolved until the DIB phenomena can be truly reproduced in laboratory spectroscopic investigations, under conditions that can be translated directly to those in the interstellar medium.

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