



Search for outer-well states above the ionization potential in H₂

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Abstract

Recent ab initio calculations by Detmer et al. [J. Chem. Phys. 109 (1998) 9694] and by Staszewska and Wolniewicz [J. Mol. Spectr. 212 (2002) 208] have produced potential energy curves in the energy region between the $n = 3$ and $n = 4$ dissociation limits in hydrogen, that in principle support bound states of an exotic nature. They are confined to large internuclear separation ($R > 10$ a.u.) by a potential barrier giving the H₂ molecule an unusually large size. In an experimental study involving a four-laser excitation scheme such states were searched for, but the dominant feature observed in this energy region is that of a direct continuum excitation when probing states of *ungerade* symmetry. An analysis in terms of a Landau–Zener tunneling model predicts that all vibrational levels in the $6^1\Sigma_u^+$ state, perhaps with exclusion of the $v = 0$ level, are subject to rapid predissociation.

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1. Introduction

In molecular hydrogen a special class of exotic long-range valence states exists due to strong avoided crossings between potential energy curves. For the manifold of *gerade* symmetry these states were known for decades. Davidsson [1] recognized the double-well structure of the second $1^1\Sigma_g^+$ state (EF). While the third state of $1^1\Sigma_g^+$ symmetry (GK) has a small internal barrier [2], a much larger barrier was predicted for the next $1^1\Sigma_g^+$ state (HH) by Wolniewicz and Dressler [3]. A breakthrough in the experi-

mental study of outer-well states was accomplished by the introduction of XUV-multiple resonance studies [4,5]. Not only did it become possible to enter the Franck–Condon forbidden region, also the preparation of well-assigned intermediate quantum states facilitated the interpretation of observations. As for the states of *ungerade* symmetry Dabrowski and Herzberg [6] had predicted, from early spectroscopic observations, that the third $1^1\Sigma_u^+$ state ($B''\bar{B}$) exhibits a double well structure. Single quantum levels in the \bar{B} outer well state were recently probed in a four-laser experiment by de Lange et al. [5]. The observations of high-lying exotic valence states were accompanied by refined ab initio calculations including relativistic effects for the $4(H\bar{H})^1\Sigma_g^+$ [7] and $3(B''\bar{B})^1\Sigma_u^+$ states [5] reproducing level energies to within 1 cm^{-1} .

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The question arises whether higher lying double-well structures exist and if so, support bound states. Detmer et al. [8] calculated Born–Oppenheimer potential curves of several higher lying states of ${}^1,3\Sigma_{g,u}^+$ symmetries. These calculations predict an internal barrier behavior for the $4^1\Sigma_u^+$ and $5^1\Sigma_u^+$ states, but the $6^1\Sigma_u^+$ state is particularly interesting from an experimentalist's perspective; it contains a large barrier and an outer well part which is bound by more than 5000 cm^{-1} at $30\text{--}35\text{ a.u.}$ At $R > 36\text{ a.u.}$ the potential follows the $\text{H}^+\text{--}\text{H}^-$ ion-pair curve. While the calculations of Detmer et al. [8] already gave a guide for the experimentalist, Staszweska and Wolniewicz [9] recently presented a highly accurate BO-curve for the $6^1\Sigma_u^+$ state, adiabatic corrections, a calculation of level energies in $6^1\Sigma_u^+$, and a tabulation of Franck–Condon factors (FCF) for the $6^1\Sigma_u^+\text{--}\text{H}\bar{\text{H}}^1\Sigma_g^+(v', v'')$ system, suggesting possibilities for excitation of the high-lying $6^1\Sigma_u^+$ outer well state.

In this paper we present our findings on an experimental search for bound states in the outer well of the $6^1\Sigma_u^+$ state. For reasons discussed the excitation path $\text{X}^1\Sigma_g^+(v=0)\text{--}\text{B}^1\Sigma_u^+(v=15)\text{--}\text{I}^1\Pi_g(v=2)\text{--}6^1\Sigma_u^+(v=0)$ was followed, but no narrow features related to $6^1\Sigma_u^+$ were observed. Led by these experimental findings an analysis of the dynamical behavior of the higher lying outer well states in H_2 was performed, including the phenomenon of tunneling-predissociation.

2. A scheme for excitation of the $6^1\Sigma_u^+$ state

In Fig. 1 the potential energy curves for ${}^1\Sigma_u^+$ states ($n \geq 3$), relevant for this study, are reproduced from [8]. We focus on states of *ungerade* symmetry, because excitation schemes via lower lying states of *gerade* symmetry are more suitable for our experimental setup. For the same reason of experimental accessibility we consider only *singlet* states.

Based on the potential energy curve of [8] for the $6^1\Sigma_u^+$ state bound state energy levels in the outer well were calculated for $v = 0\text{--}70$ using the LEVEL computer code, developed by Le Roy [10]. The $6^1\Sigma_u^+$, $v = 0$, $J = 0$ is predicted at $133\,640\text{ cm}^{-1}$, in agreement with the finding of [9]. In order

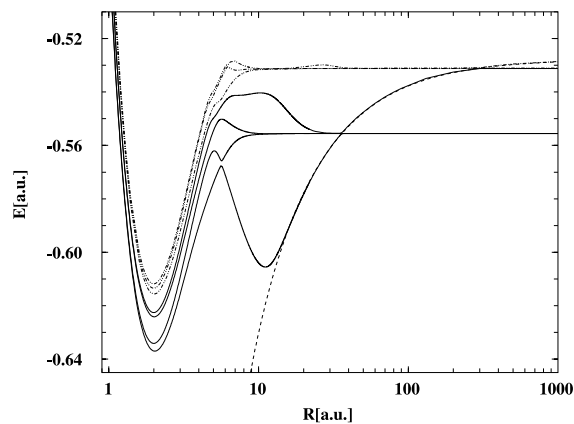


Fig. 1. Potential energy curves for states of ${}^1\Sigma_u^+$ symmetry in hydrogen. The lowest full curve represents the $\text{B}'\bar{\text{B}}$ or $3^1\Sigma_u^+$ state, while the next three higher full curves represent $4, 5, 6^1\Sigma_u^+$. The dotted lines represent the $7, 8, 9^1\Sigma_u^+$ states. The dashed curve represents the H^+H^- pure Coulombic potential. On this scale the avoided crossing at $R = 36\text{ a.u.}$ is not visible. Picture kindly provided by the authors of [8] and reproduced with permission.

to predict excitation spectra, FCF were calculated for excitation schemes involving the most appropriate intermediate levels of *gerade* symmetry, again using the LEVEL computer code [10], the potential energy curve of $6^1\Sigma_u^+$ as reported in [8], and the potential energy curves of the $\text{H}\bar{\text{H}}^1\Sigma_g^+$ state [7]. As a result we find that the lower vibrational levels in the $6^1\Sigma_u^+$ state can only be reached, with reasonable FCF, from those vibrational levels in the $\bar{\text{H}}^1\Sigma_g^+$ outer well state ($v_{\text{H}} > 30$), that are subject to rapid autoionization [11]. This is confirmed by the Franck–Condon calculations reported by Staszweska and Wolniewicz [9]. Even in excitation from a vibrational level as high as $\text{H}\bar{\text{H}}^1\Sigma_g^+$, $v = 15$, the FCF to the lowest v level in $6^1\Sigma_u^+$ is only on the order of 10^{-15} . Because the low vibrational levels should be searched for, as discussed below, the $\text{H}\bar{\text{H}}^1\Sigma_g^+$ state seems not to be the appropriate intermediate state for an experimental study of $6^1\Sigma_u^+$.

Along the same lines we performed Franck–Condon calculations with transitions originating in the lowest four vibrational levels in the shallow $\text{I}^1\Pi_g$ potential, which is bound by 200 cm^{-1} below the $\text{H}(n=2)$ dissociation limit [12]. The isolated outer well is referred to as $\text{I}^1\Pi_g$. The results are listed in Table 2 for excitation to the lowest ten

v levels in $6^1\Sigma_u^+$ and some higher ones. In excitation from the two lowest vibrational levels in the $I^1\Pi_g$ state the overlap to $6^1\Sigma_u^+$, $v' = 0$ is still small: 10^{-14} for $v'' = 0$ and 10^{-8} for $v'' = 1$. But for the next two vibrations the Franck–Condon intensity becomes favorable: 9×10^{-4} for $v'' = 2$ and 2×10^{-1} for $v'' = 3$. The $v'' = 3$ level in the I' outer well lies very close to the $n = 2$ dissociation limit, and although some spectral lines in the neighborhood were observed, no unambiguous assignments for $v'' = 3$ could be made, unfortunately [4]. The $v'' = 2$ level is therefore taken as the starting level for further excitation to probe $6^1\Sigma_u^+$, $v' = 0$. The excitation energy of $I^1\Pi_g$, $v = 2$, $J = 1$ is $118359.00 \text{ cm}^{-1}$ [4].

The above calculation of energy levels, and also those of [9] suggest that the resonances are sharp and associated with bound levels. However, the avoided crossing at 36 a.u. will allow for tunneling, resulting in intramolecular decay, associated with broadening of the resonances. This phenomenon is here treated in a Landau–Zener model, describing the motion of a particle on a crossing of two interacting potential curves. The $4^1\Sigma_u^+$ and $5^1\Sigma_u^+$ states lie in between the $3^1\Sigma_u^+$ and $6^1\Sigma_u^+$ states; their potential energy curves are represented by straight horizontal lines in the crossing region, while the $3^1\Sigma_u^+$ and $6^1\Sigma_u^+$ states exhibit the typical anti-crossing behaviour. Hence the assumption is made that the dominant interaction occurs between the $3^1\Sigma_u^+$ and $6^1\Sigma_u^+$ states, and the model is simplified by neglecting the role of $4^1\Sigma_u^+$ and $5^1\Sigma_u^+$ states.

The Landau–Zener tunneling probability is given by [13]:

$$p = \exp\left(-\frac{2\pi V^2}{\hbar v |F_1 - F_2|}\right), \quad (1)$$

where the F_i can be interpreted as the forces acting on the particle moving on potentials i at the crossing point R_0 , that can be expressed as:

$$F_i = -\left.\frac{\partial V_i}{\partial R}\right|_{R=R_0}. \quad (2)$$

The forces F_i are derived from the slopes of the asymptotes (diabatic potentials), whereas the interaction energy V is derived from the gap ($\Delta = 2V$) at the avoided crossing. The recent

potential curves of Staszewska and Wolniewicz [9] give an interaction strength V of 40 cm^{-1} . The velocity v is derived from the boundary condition given by the initial kinetic energy of the particle:

$$v = \sqrt{\frac{2}{m}[E_{\text{vib}} - V_{\text{adiabatic}}(R_0)]}. \quad (3)$$

The tunneling probability p , which is dependent on the shapes of the potentials and the gap at the crossing point R_0 , can be used to calculate broadening in the excitation spectrum. Line broadening parameters Γ (FWHM), as listed in Table 1, can be calculated by taking a total probability of $p(2-p)$ for the loss rate per vibration (probability p for outward travel and $p(1-p)$ for inward tunneling), with neglect of secondary processes. It should be mentioned here that the vibrational level $v = 0$ cannot be treated in the Landau–Zener model, because the energy level lies below the value of the adiabatic curve at R_0 , giving a negative kinetic energy from which no classical velocity can be calculated. A crucial result of these calculations is that the predissociation rate increases with vibrational quantum number in $6^1\Sigma_u^+$. That is the reason why a search for bound features in this potential should focus on the low v region and if possible on the $v = 0$ level, which may be expected to be the narrowest, although its actual width cannot be calculated in the model presented here.

Excitation spectra from the $I^1\Pi_g$, $v = 2$ intermediate state are obtained using the calculated line broadening parameters $\Gamma(v)$ and FCF from Table 2; possible radial-dependent transition dipole moments are neglected in these calculations. Results are plotted in Fig. 2 for two different values of V , to explore the sensitivity of this parameter for the

Table 1
Tunneling probability p and linewidth Γ for different values of the interaction parameter V and for the vibrational levels $v = 1$ and $v = 2$ in the $6^1\Sigma_u^+$ state

$V \text{ (cm}^{-1}\text{)}$	$v = 1$		$v = 2$	
	p	$\Gamma \text{ (cm}^{-1}\text{)}$	p	$\Gamma \text{ (cm}^{-1}\text{)}$
35	0.68	39.7	0.79	54.1
50	0.46	21.2	0.62	33.5
65	0.27	10.8	0.45	20.4
80	0.14	5.1	0.30	12.1

Table 2
FCF for the $6^1\Sigma_u^+ - \Pi'\Pi_g(v', v)$ system

v'	$v = 0$	$v = 1$	$v = 2$	$v = 3$
0	9.5(-15)	2.9(-8)	8.7(-4)	2.2(-1)
1	1.8(-13)	2.3(-7)	2.1(-3)	9.2(-2)
2	1.5(-12)	9.2(-7)	4.0(-3)	1.4(-1)
3	7.9(-12)	2.6(-6)	5.9(-3)	6.7(-2)
4	3.1(-11)	5.9(-6)	8.3(-3)	9.2(-2)
5	9.9(-11)	1.2(-5)	1.0(-2)	4.1(-2)
6	2.7(-10)	2.0(-5)	1.3(-2)	6.1(-2)
7	6.3(-10)	3.3(-5)	1.4(-2)	2.2(-2)
8	1.4(-9)	5.0(-5)	1.6(-2)	4.0(-2)
9	2.7(-9)	7.3(-5)	1.8(-2)	1.1(-2)
10	5.0(-9)	1.0(-4)	1.9(-2)	2.4(-2)
20	3.5(-7)	8.8(-4)	2.5(-2)	1.4(-4)
30	4.3(-6)	2.7(-3)	1.9(-2)	1.9(-3)
40	2.7(-5)	5.8(-3)	1.1(-2)	3.4(-3)

The value in parentheses refers to the exponent 10^{-a} .

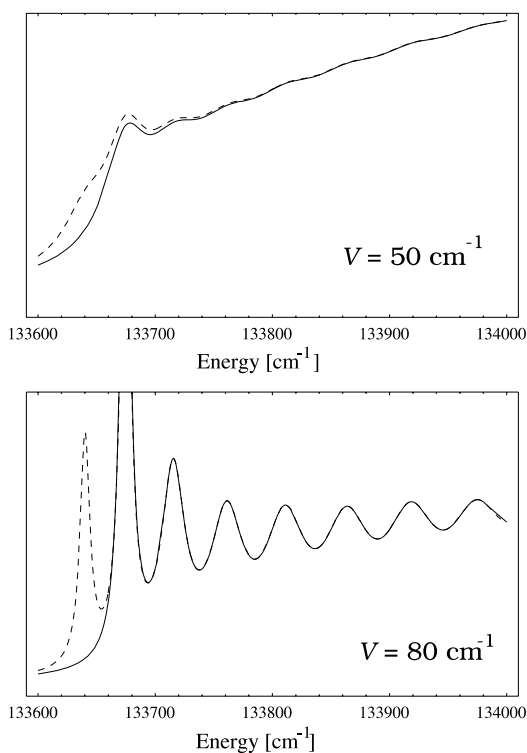


Fig. 2. Simulated spectra originating in the $\Pi'\Pi_g$, $v'' = 2$ state in excitation to the $6^1\Sigma_u^+$ state for values of the interaction parameter V as indicated. The horizontal axis represents the excitation energy above the $X^1\Sigma_g^+$, $v = 0$, $J = 0$ ground state. The contribution of the $v' = 0$ is given separately by the dashed line.

resulting excitation spectrum. The dashed line represents the contribution of the $6^1\Sigma_u^+$, $v = 0$ level with a value for Γ taken as that of $v = 1$. At an interaction parameter of $V = 80 \text{ cm}^{-1}$ a clear oscillation pattern results, while at a value of $V = 50 \text{ cm}^{-1}$ the vibrational structure in the excitation spectrum is almost fully washed out and the contribution of the $v = 0$ level does not significantly change the onset of the signal at the low frequency side. For the recent ab initio value of $V = 40 \text{ cm}^{-1}$ the oscillations will be slightly more diffuse than in the case of the graph calculated for $V = 50 \text{ cm}^{-1}$. Of importance for the evaluation of results is the slope of the signal increase above the $n = 3$ dissociation threshold. In cases of very broad lineshapes the tails at the low frequency side extend to energies below the $n = 3$ dissociation limit, which is at 133610.3 cm^{-1} . That part of the result should be considered unphysical. In the model tunneling leads to predissociation and that process can only occur for excitation above the $n = 3$ threshold.

3. Experimental setup and results

The experimental setup is essentially the same as the one used for the excitation of bound levels in the $B''B^1\Sigma_u^+$ state [5]. The levels in the $6^1\Sigma_u^+$ state are excited in a multiple-resonance scheme as

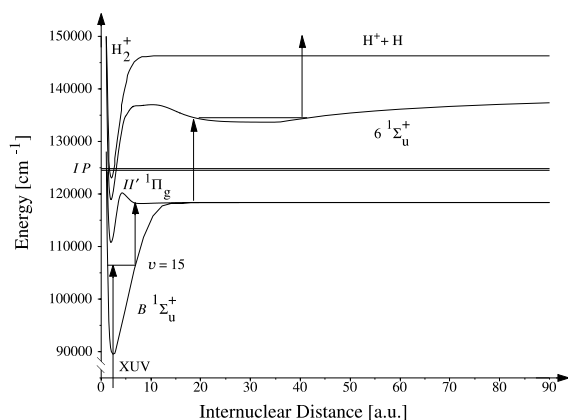


Fig. 3. Four-photon pump-probe excitation scheme for the study of $6^1\Sigma_u^+$ outer well states.

shown in Fig. 3. First a pulsed and tunable XUV radiation excites population in the $B^1\Sigma_u^+$, $v = 15$ state and subsequently a tunable pulsed laser in the 850 nm range further excites H_2 molecules to the $I'^1\Pi_g$, $v = 2$, $J = 1$ level. The first two pulses, XUV and near-IR, arrive simultaneously in the interaction zone in view of the short (1 ns) lifetime of the B state and the duration of the pulses (5 ns). In this way population is created with a vibrational distribution confined to the I' outer well. A third laser pulse, tunable in the red wavelength region, is then applied to enter the energetic range just above $133\,600\text{ cm}^{-1}$, where levels in the $6^1\Sigma_u^+$ outer well are expected. A fourth laser pulse at 532 nm serves as a tool to generate signal (H^+ -ions) whenever a bound state is excited by the third laser; the population in the $6^1\Sigma_u^+$ outer well is further promoted to the range above the dissociation threshold of the H_2^+ ion.

However, it should be realized that the 532 nm probe laser also produces H^+ if dissociation into the $H(n = 3)$ channel occurs. So the detection scheme is not able to distinguish between the generic signal of bound outer well states in the neutral H_2 molecule ($6^1\Sigma_u^+$) and the secondary signal from $H(n = 3)$ products.

In Fig. 4 an excitation spectrum near the $n = 3$ threshold is shown. The spectrum is somewhat hampered by noise, although several noise-reducing measures were taken. Part of the intensity fluctuations of the H^+ signal, appearing as noise in

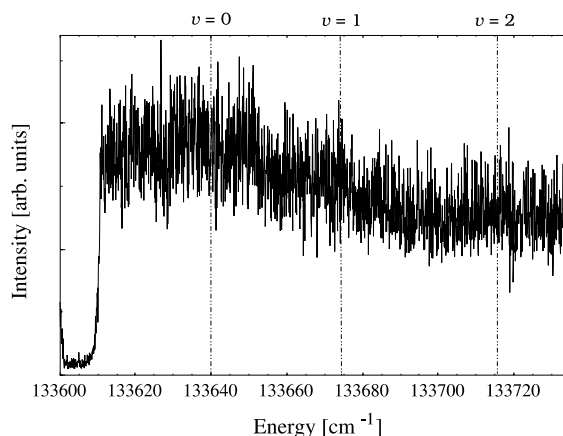


Fig. 4. Sum of seven spectra in excitation from the $I'^1\Pi_g$, $v = 2$, $J = 1$ intermediate state following the four-laser scheme of Fig. 3. The dotted vertical lines indicate the positions of $v = 0, 1$ and 2 levels in $6^1\Sigma_u^+$.

Fig. 4 is a result of multi-photon transitions originating in the $I'^1\Pi_g$ intermediate state. The bandwidth of the third laser providing the tuning wavelength is 0.3 cm^{-1} . The three-photon excitation energy is obtained by adding the accurately known level energy of the intermediate I' , $v = 2$, $J = 1$ state to the frequency of the third photon yielding an accuracy of 0.3 cm^{-1} for the total excitation energy.

In addition to the measurements performed with $I'^1\Pi_g$, $v = 2$ as intermediate, also recordings of excitation spectra taken with $I'^1\Pi_g$, $v = 0$ and $v = 1$ as intermediate state were taken. The results carry the important feature of the same steep rise of signal at the total excitation energy of $133\,610\text{ cm}^{-1}$.

4. Discussion and conclusion

The observed spectra originating from the $I'^1\Pi_g$, $v = 2$ state exciting the region above the $n = 3$ dissociation threshold do not show the patterns predicted by ab initio calculations of the bound state energies, combined with Landau–Zener calculations of the resonance widths as shown in Fig. 2. The fact that in excitation from $I'^1\Pi_g$, $v = 0$ and $v = 1$ intermediate states a similar onset is observed is in contradiction with the

calculations of FCF, which show that the probability of excitation at $133\,640\text{ cm}^{-1}$ is negligible from these intermediate states. Hence it is concluded that neither the $6^1\Sigma_u^+$, $v = 0$ resonance, located at $133\,640\text{ cm}^{-1}$ and indicated by a vertical dashed line in Fig. 4, nor any other of the vibrational resonances in $6^1\Sigma_u^+$ is observed.

A prominent feature in the spectrum of Fig. 4 is the sharp onset, less than 1 cm^{-1} wide, right at the value of the dissociation limit at $133\,610.3\text{ cm}^{-1}$. A possible interpretation of this feature is direct excitation of the continuum above the $n = 3$ limit. This onset is similar to that observed in a two-photon excitation study where the continuum of *gerade* symmetry above the $n = 3$ threshold is reached in excitation via the $B^1\Sigma_u^+$ state [14]. Within the $1^1\Sigma_u^+$ manifold the $4^1\Sigma_u^+$ state exhibits a continuum, that could be excited from the $I^1\Pi_g$ state; this excitation channel would in principle give a sharp onset at the dissociation limit. The $5^1\Sigma_u^+$ is an alternative candidate to yield the onset in electronic excitation. However, the relatively high barrier at 6 a.u. [8,9] will shift the onset of excitation towards higher energy and hence the $5^1\Sigma_u^+$ state cannot account for a sharp onset. Continua of $1^1\Pi_u$ and $1^1\Delta_u$ symmetry could also produce a steep ascent; information on such states in this energy region is not available. We conclude that continuum states dominate the spectrum presently observed and the spectrum does not correspond to the $6^1\Sigma_u^+ - I^1\Pi_g(v, 2)$ bands.

As an outlook we note that the $I^1\Pi_g$, $v = 3$ level would be ideally suited to excite the lower vibrational levels in the $6^1\Sigma_u^+$ state. The FCF for excitation of $6^1\Sigma_u^+$, $v = 0$ reaches a maximum value of 0.22. Hence excitation via $I^1\Pi_g$, $v = 3$ would give a transition strength, more than two orders of magnitude larger than for $I^1\Pi_g$, $v = 2$. Moreover the $6^1\Sigma_u^+$, $v = 0$ state, the one with supposedly the longest lifetime, would be excited with the largest probability. This transition strength is likely to be stronger than that of the direct excitation of the continuum as observed in the present experiment. The problem is that $I^1\Pi_g$, $v = 3$ levels could not be assigned so far [4], but some very weak resonances just below (within 1 cm^{-1}) the $n = 2$ threshold were observed; these might be associated with $I^1\Pi_g$, $v = 3$. Further

investigation of these resonances might lead to identification of $I^1\Pi_g$, $v = 3$ levels, and hence pave the way for excitation of the $6^1\Sigma_u^+$, $v = 0$ level.

The calculation on the intramolecular tunneling predissociation at the crossing at 36 a.u., however, suggests that neither of the levels in $6^1\Sigma_u^+$, perhaps with the exception of $v = 0$, gives rise to a narrow resonance. It is noted that the tunneling model relies on a simplified two-state Landau–Zener analysis. A full treatment of the four-channel problem for the 3, 4, 5, $6^1\Sigma_u^+$ states, with inclusion of radial-dependent electronic transition moments, might produce a more accurate picture of the dynamics at the 36 a.u. crossing.

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