Contrasting Singlet−Triplet Dynamical Behavior of Two Vibrational Levels of the Acetylene S_1 $2^1 3^1 B^2$ Polyad[†]

Wilton L. Virgo, Kyle L. Bittinger, Adam H. Steeves, and Robert W. Field*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Surface electron ejection by laser-excited metastables (SEELEM) and LIF spectra of acetylene were simultaneously recorded in the regions of the $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$ nominal $2^1 3^1 4^2$ $K_a = 1 \leftarrow 0_0$ and $2^1 3^1 6^2$ $K_a = 1 \leftarrow 0_0$ bands near 46 140 cm^{-1}. The upper states of these two bands are separated by only ~100 cm^{-1}, and the two S_1 vibrational levels are known to be strongly mixed by anharmonic and Coriolis interactions. Strikingly different patterns were observed in the SEELEM spectra in the regions of the $2^1 3^1 4^2$ and $2^1 3^1 6^2$ vibrational levels. Because the equilibrium structure of the T_3 electronic state is known to be nonplanar, excitation of ν_4 (torsion) and ν_6 (antisymmetric in-plane bend) are expected respectively to promote and suppress vibrational overlap between low-lying S_1 and T_3 vibrational levels. The nearly 50:50 mixed $2^1 3^1 4^2 - 2^1 3^1 6^2$ character of the S_1 vibrational levels rules out this simple Franck−Condon explanation for the different appearance of the SEELEM spectra. A simple model is applied to the SEELEM/LIF spectra to explain the differences between spectral patterns in terms of a T_3 doorway-mediated singlet−triplet coupling model.

Introduction

Surface electron ejection by laser-excited metastables[1−3] (SEELEM) and LIF spectroscopy are complementary tools that have been used to gain insight into singlet−triplet interactions in the $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ (S_1-S_0) electronic spectrum of acetylene, C_2H_2.[3−6] LIF detection is limited to short-lived ($\tau_{\text{radiative}} < 10$ μs), strongly fluorescing singlet states, and SEELEM detection is sensitive only to long-lived ($\tau > 300$ μs) states with vertical electronic excitation above a threshold energy set by the work function of the metal used as the SEELEM detector surface. Therefore, SEELEM and LIF detection channels observe mutually exclusive sets of eigenstates that arise from spin−orbit mixed S_1,$T_{3,2,1}$ zero-order basis states. A comparison of simultaneously recorded SEELEM and LIF spectra reveals features of electronic structure and photochemical pathways that are invisible via traditional, single-channel spectroscopic probes such as LIF alone, REMPI, phosphorescence, phosphor surface, etc.[7,8] The information gained from comparison of acetylene SEELEM/LIF spectra can yield a mechanistic description of singlet−triplet interaction and holds promise for describing the structure and dynamics of other small polyatomic species.[9,10] Dupré et al.[11,12] have determined that the singlet−triplet dynamics of acetylene near the region of the $\tilde{A}^1A_u$ state are governed by a doorway mediated mechanism,[3−6,13] where particular vibrational levels of the T_3 state provide a doorway for intersystem crossing between the initially excited S_1 bright state and the dense manifold of dark $T_{1,2}$ states.

The $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$ electronic band system of acetylene is one of the most thoroughly examined electronic transitions of any polyatomic molecule.[14−19] Despite numerous investigations, only a partial picture of $\tilde{A}^1A_u$-state vibrational structure and interactions has been developed. Several researchers have used double resonance techniques to detect and analyze transitions to the ν_4 and ν_6 fundamentals, overtones, and combination bands in the $\tilde{A}^1A_u$ state. Utz et al. were the first to unambiguously assign electronic transitions to the $\tilde{A}^1A_u$-state ν_4 (torsion) and ν_6 (antisymmetric in-plane bend) vibrational fundamentals using pulsed laser double resonance in a room-temperature cell.[20] They observed strong *a*- and *b*-axis Coriolis interactions between the two nearly degenerate bending modes, and deperturbed these interactions to obtain vibrational frequencies, Coriolis interaction constants, and rotational constants. That experiment is very relevant to the work presented in this paper, because the near degeneracy of the two vibrational fundamentals is expected to result in analogous interactions among the higher lying combination and overtone levels involving ν_4 and ν_6.[21] Mizoguchi et al., also observed *ungerade* vibrational states via the $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$ transition using IR-UV double resonance spectroscopy.[22] In particular, they excited acetylene to its *ungerade* $n\nu_3' + \nu_4'$ and $n\nu_3' + \nu_6'$ ($n = 2, 3$) vibrational levels in the $\tilde{A}^1A_u$ state via IR excitation of selected rotational levels in the ν_3'' vibrational state of the $\tilde{X}^1\Sigma_g^+$ electronic ground state. They investigated the Coriolis coupling between the combination bands involving ν_4' and ν_6' and examined the vibrational mode dependence of the singlet−triplet interaction by observing splittings in the $K_a = 1$ rotational levels of the $3\nu_3' + \nu_6'$ band. The singlet−triplet interaction in these states was further probed in continuing work by Yamakita and Tsuchiya,[23] who observed Zeeman quantum beats by IR-UV double resonance LIF. They observed both rotational level splittings and Zeeman quantum beats in the fluorescence decay of the $3\nu_3' + \nu_6'$ band. No analogous splitting or Zeeman quantum beats were seen in the $3\nu_3' + \nu_4'$ band. They concluded that excitation of the out-of-plane ν_4' torsional mode suppresses the singlet−triplet interaction and excitation of the in-plane antisymmetric bend, ν_6', promotes S_1-T_3 interaction. From this, it was inferred that the singlet−triplet mixing occurs in a planar (C_{2h} or C_{2v}) geometry rather than at a nonplanar C_2 geometry, because the $3\nu_3' + \nu_4'$ band did not exhibit any rotational line splittings or Zeeman quantum beats.

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* Corresponding author. E-mail: rwfield@mit.edu.

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The focus of this paper is a comparison of combination bands involving overtones of the low-frequency bending vibrations, ν_4 and ν_6, of acetylene in its $\tilde{A}^1A_u$ state. In the normal mode model of acetylene vibrational dynamics, ν_4 is the only normal vibration in the $\tilde{A}^1A_u$ state that involves a motion out-of-the-plane from the planar, trans-bent equilibrium structure of the $\tilde{A}$ state, and ν_6 is an in-plane antisymmetric bend. A more sophisticated polyad model[24] goes beyond the zero-order normal mode picture by incorporating anharmonic and vibration−rotation (including Coriolis) interactions among groups of near degenerate states. The results of such an analysis show that the resultant eigenstates formed from the zero-order degenerate bending modes are profoundly mixed via strong anharmonic (Darling−Dennison) and Coriolis interactions.[25] In this case, the simpler normal mode model is invalid, and the vibrational wavefunctions of levels assigned to ν_4 or ν_6 do not resemble the nuclear motions suggested by their labels, but are strongly mixed superpositions of the two zero-order bending modes. In this work, the nominal 4^2 and 6^2 spectral labels are retained, despite the fact that the two levels are nearly 50:50 mixed.

We report on the simultaneously recorded SEELEM and LIF spectra that sample the near-degenerate, strongly mixed $2^13^14^2$ $K_a = 1$ and $2^13^16^2$ $K_a = 1$ vibrational levels of acetylene in its $\tilde{A}^1A_u$ state. The SEELEM spectra of these two vibrational levels are remarkably different. The spectra provide a unique opportunity to investigate the effect of selective vibrational excitation on the interaction between singlet and triplet states of acetylene. One might expect the intensities in the SEELEM spectra of the $2^13^14^2$ and $2^13^16^2$ vibrational levels to be controlled by Franck−Condon overlap between the vibrational wavefunctions of the interacting S_1 and T_3 electronic states. The expectation under a normal mode model is that, because the T_3 electronic state has a nonplanar C_s configuration,[26,27] excitation of the in-plane ν_6 mode would result in small vibrational overlap with T_3, and excitation of the out-of-plane vibration, ν_4, would result in large vibrational overlap. If the normal mode model were valid, interaction with triplet states would be promoted by excitation of ν_4, resulting in large SEELEM signal, and excitation of ν_6 should suppress SEELEM activity. The strongly mixed nature of the $\tilde{A}^1A_u$ $2^13^14^2$ $K_a = 1$ and $2^13^16^2$ $K_a = 1$ vibrational levels rules out such a simple explanation for the contrasting SEELEM spectra observed in the experiment. The purpose of this paper is to provide an explanation of the difference between the SEELEM spectra involving the mixed $2^13^14^2$ and $2^13^16^2$ vibrational levels, and to propose a qualitative mechanism that gives rise to the different spectral patterns. Comparison and analysis of the SEELEM/LIF spectra will elucidate the mechanism of the doorway S_1−T_3 interaction process.

Experiment

SEELEM is a versatile and sensitive technique for investigating “dark” (weakly fluorescing) metastable molecules produced via laser excitation.[1−6] In the SEELEM experiment, a molecular beam of acetylene is excited by a ∼5 ns pulsed laser into spin−rotation−vibration eigenstates of metastable electronic states via weak, nominally forbidden transitions. After excitation, the long-lived species must travel 35 cm before colliding with an Au metal detector surface, where an electron is ejected in a de-excitation process. Two criteria must be met for electron ejection by a metastable species. First, the vertical electronic energy of the metastable (T_3) approaching the surface must exceed the work function of the metal ($\Phi_{Au} = 5.1$ eV). Second, the radiative lifetime of the detected metastable eigenstate ($\tau_{radiative}$) must exceed the flight time from the point of laser excitation to the SEELEM surface ($\Delta t = 300\ \mu s$).

A sample of acetylene (BOC gases) at a backing pressure of 1 atm was pulsed through a 0.5 mm diameter nozzle operating at 10 Hz into a diffusion pumped vacuum chamber at $\sim 5 \times 10^{-5}$ Torr. An Nd:YAG pumped, frequency-doubled dye laser (220 nm) excited the acetylene molecules in the pulsed jet expansion 2 cm downstream from the nozzle orifice. UV-LIF was detected perpendicular to the plane defined by the intersection of the pulsed molecular and laser beams using *f*/1.2 collection optics, a fluorescence filter (UG-11) to reduce scattered laser light, and a PMT (Hamamatsu model R375). The fluorescence signal was averaged by a boxcar integrator and recorded. For SEELEM detection, the excited molecules in the pulsed expansion passed through a conical skimmer (3 mm diameter) to form a collimated molecular beam, which traveled into a differentially pumped detector chamber maintained at $\sim 4 \times 10^{-7}$ Torr, and collided with a heated (300 °C) Au metal surface 35 cm downstream from the point of laser excitation. The SEELEM detector was identical to that used in the previously described apparatus with Au foil ($\Phi = 5.1$ eV) as the metal surface.[4] Particle counting techniques, including a multichannel scalar (Oxford Tennelec Nucleus Inc. MCS-II v2.091) were used to record laser-excited metastable counts as a function of laser frequency, along with the simultaneously recorded LIF spectra. Both SEELEM and LIF signals were averaged over 100 laser shots/data point.

Observations

Figure 1a shows the SEELEM (plotted upward) and LIF (plotted downward) spectra for the $\tilde{A}^1A_u$−$\tilde{X}^1\Sigma_g^+$ nominal $2^13^14^2$ $K_a = 1 \leftarrow 0_0$ Q and R branch rovibronic transitions of acetylene near 46 195 cm^{-1}. The SEELEM and LIF spectra are very similar for this band in terms of both frequencies and relative intensities, with the exception of the anomalously weak LIF Q(1) feature. Each SEELEM feature in the spectrum is localized in energy near an LIF partner feature. No splitting of the rotational lines in the LIF spectrum is observed at the 0.06 cm^{-1} resolution.

Figure 1b presents the SEELEM/LIF spectra for the $\tilde{A}^1A_u$−$\tilde{X}^1\Sigma_g^+$ nominal $2^13^16^2$ $K_a = 1 \leftarrow 0_0$ P, Q, and R branch transitions near 46 090 cm^{-1}. The SEELEM spectrum of $2^13^16^2$ is remarkably different from that of $2^13^14^2$. The overall SEELEM signal in $2^13^16^2$ is weaker than that of $2^13^14^2$ by nearly a factor of 3, even though the LIF intensity in $2^13^16^2$ is a factor of 3 stronger than that of $2^13^14^2$. In $2^13^16^2$, the SEELEM features are not well correlated in intensity with the corresponding features in LIF. In fact, in several cases where a strong LIF feature appears, the partner SEELEM feature is near or completely below the noise level. The observed pattern of SEELEM features in $2^13^16^2$ suggests a significant J' dependence to the SEELEM activity and, hence, to the interaction of the bright singlet state, S_1, with the perturbing triplet state, T_3.

Analysis of S_1 $2^13^1B^2$ Interactions

Although spectra involving vibrational excitation have been traditionally analyzed in terms of normal modes, it is well-known that at significant excitation energy, the modes can become strongly mixed, and large deviations from the small-amplitude, rigid-molecule normal vibrations are expected. In the case of the ν_4 and ν_6 bending vibrations of $\tilde{A}$-state acetylene, the pure normal mode description is not adequate. Superpositions of normal modes are required to describe the wavefunctions of levels involving the low-frequency excited-state bending vibrations.[20,25]

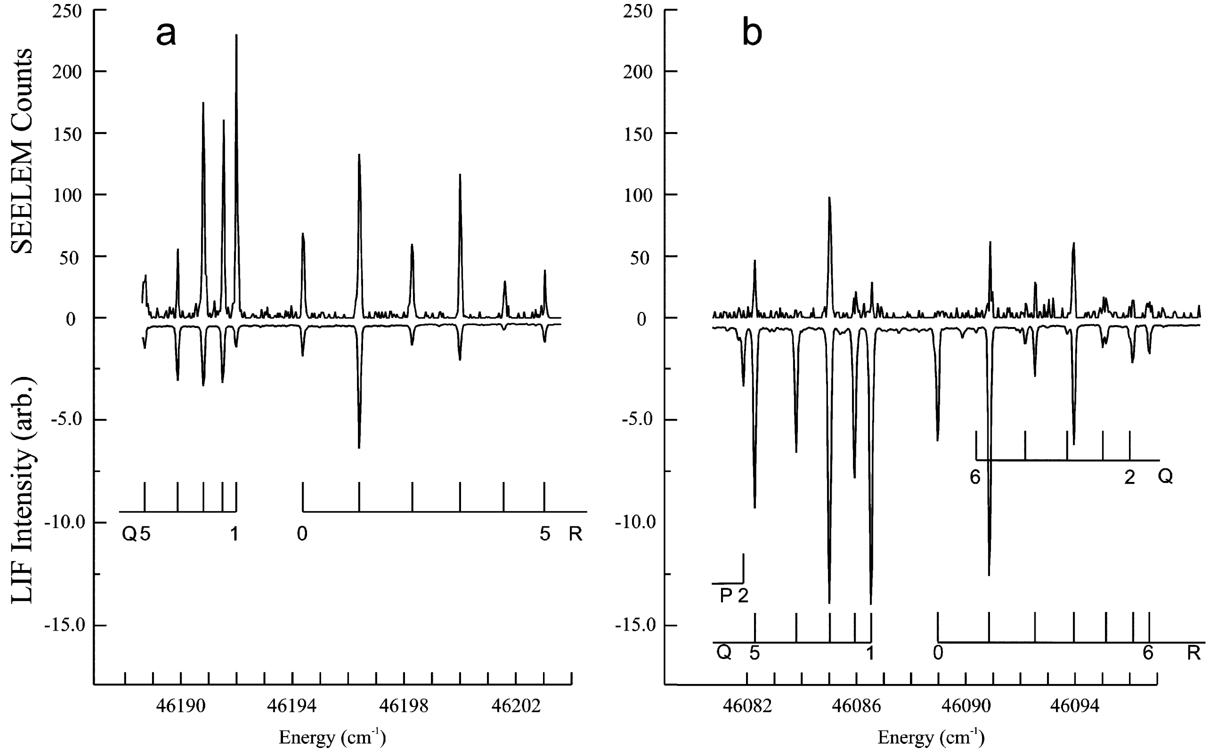

Figure 1. (a) Simultaneously recorded surface electron ejection by laser excited metastables (SEELEM, upper trace) and ultraviolet laser-induced fluorescence (UV-LIF, lower trace) spectra of the $2^1 3^1 4^2$ $K_a = 1$ sublevel of the $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$ electronic transition. (b) P, Q, and R branch features of the SEELEM and LIF spectra of the $2^1 3^1 6^2$ $K_a = 1$ sublevel. The weak Q branch features, which are overlapped with the *R* branch features of $2^1 3^1 6^2$ $K_a = 1$, belong to a sublevel of a different polyad.

Though no deperturbation of the $2^1 3^1 B^2$ polyad has been attempted, the qualitative structure of the polyad can be anticipated by drawing parallels to the B^2 polyad, which has recently been analyzed by Merer et al.[25] In that work, an effective, multiresonant Hamiltonian was constructed to take into account the effects of Darling-Dennison resonance in addition to the *a*- and *b*-axis Coriolis interactions described by Utz and co-workers.[20] This effective Hamiltonian was fitted to the available experimental data from the high-sensitivity LIF spectra of the B^2 polyad (containing the 4^2 (a_g), 6^2 (a_g), and $4^1 6^1$ (b_g) basis states) recorded in a molecular beam. It was found that the strength of the Darling−Dennison interaction is sufficient to cause nearly complete (~50:50) mixing of the 4^2 and 6^2 basis states in the $J = K_a = 0$ levels. In the absence of other effects, the nominal 4^2 and 6^2 levels would contain the same fractional contributions from the 4^2 and 6^2 basis states and would only differ in the phase of that mixing. The $4^1 6^1$ state remains essentially pure in $J = K_a = 0$.

For levels with $J > 0$, the Coriolis interactions must be considered. In particular, we focus on the $K_a = 1$ sublevels that, as a consequence of the *c*-type selection rules for the $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$ transition, dominate the LIF spectrum recorded from the ground ($l'' = 0$) vibrational level. In $K_a = 1$, the 2:2 Darling−Dennison interaction strongly mixes the near-resonant 4^2 and 6^2 zero-order levels, as it does in $K_a = 0$. However, in $K_a = 1$, the *a*-axis Coriolis matrix elements now connecting the $4^1 6^1$ state to the 4^2 and 6^2 basis states have opposite phases. If the Darling−Dennison interaction is prediagonalized, the phases of the Coriolis matrix elements result in a strong interference effect. The nominal 4^2 level has the proper phase to mix strongly with the $4^1 6^1$, b_g vibrational symmetry level, whereas the nominal 6^2 level has the wrong phase.

Extending this argument to the $2^1 3^1 B^2$ polyad, the strongly mixed nature of $2^1 3^1 4^2$ and $2^1 3^1 6^2$ permits $2^1 3^1 4^1 6^1$ to interact with only one of the two mixed vibrational levels. An analysis of this interference effect, which depends on the relative phase of the anharmonic and Coriolis matrix elements, shows that the $2^1 3^1 4^1 6^1$ basis state is strongly Coriolis coupled to the nominal $2^1 3^1 4^2$ level but not to the nominal $2^1 3^1 6^2$ level. As a result of the interference effect, a significant amount of b_g character is mixed exclusively into $2^1 3^1 4^2$.

Although this preliminary, semiquantitative analysis is based on a local fit of the interactions within B^2, rather than a more global model for all of the S_1 bending polyads of acetylene, the interactions most pertinent to the observed SEELEM spectra can be characterized using this simple, local model.

Discussion

Even a qualitative analysis of the SEELEM spectra can reveal salient features of the singlet−triplet interaction dynamics. Despite the fact that the LIF signal in $2^1 3^1 6^2$ is a factor of 3 larger than the LIF signal of $2^1 3^1 4^2$, the corresponding SEELEM spectra do not share this same intensity ratio. In stark contrast to the LIF signal, the SEELEM signal for $2^1 3^1 6^2$ is exceedingly weak, but the $2^1 3^1 4^2$ SEELEM signal is comparatively intense. This difference in SEELEM activity can be interpreted in terms of the strength of the interaction between the bright S_1 state and a unique perturbing vibrational level of T_3.

It is known that the singlet−triplet interaction mechanism in the $\tilde{A}^1A_u$ state of acetylene is a doorway-mediated process, where the coupling of S_1 to the dark $T_{1,2}$ states is mediated by T_3.[3−6,11−13] In light of the doorway model, there are two possible explanations for the difference between the two SEELEM spectra. The first is a vibrational overlap argument, where vibrational overlap between the S_1 and T_3 vibrational wavefunctions promotes or suppresses SEELEM signal. A second possibility is that the phases of the *a*-axis Coriolis matrix elements connecting the 4^16^1 state to the 4^2 and 6^2 basis states result in an interference effect that gives rise to a difference in how the two S_1 vibrational levels interact with T_3.

In the normal mode model, ν_4 and ν_6 normal vibrations are rigorously conserved. In a more accurate polyad model, $2^13^16^2$ and $2^13^14^2$ belong to a strongly mixed superposition of modes, rather than pure normal modes. Because the vibrational levels are strongly mixed, a simple Franck−Condon argument would predict the SEELEM spectra of $2^13^16^2$ and $2^13^14^2$ to be nearly identical.

The simplest explanation for the difference between the two observed SEELEM spectra lies in an investigation of the Coriolis interaction within the mixed $2^13^1B^2$ $K_a = 1$ polyad. From the effective Hamiltonian analysis, the main difference between the wavefunctions of the two S_1 $2^13^1B^2$ vibrational levels probed in the experiment is the amount of admixed b_g vibrational character, taking into account the interference between anharmonic and Coriolis interaction matrix elements. Although $2^13^14^16^1$ is both short-lived and would fluoresce strongly, it is not easily visible in either SEELEM or LIF spectra due to low excitation probability and spectral overlap with the near degenerate 1^13^1 $K_a = 1$ level. Because the *a*-type Coriolis interaction causes $2^13^14^16^1$ to interact with (nominal) $2^13^14^2$, but not with (nominal) $2^13^16^2$, a logical conclusion is that the b_g vibrational character in the nominal $2^13^14^2$ level is what gives rise to the enhancement in SEELEM intensity. The interaction of nominal $2^13^14^2$ with T_3 is due to the mixing of b_g vibrational character into nominal $2^13^14^2$.

Although *a*-type Coriolis coupling gives rise to the SEELEM signal in the region of $2^13^14^2$ $K_a = 1$, *b*-type Coriolis coupling may contribute to the *J*-dependence of the SEELEM signal near the LIF spectrum of $2^13^16^2$ $K_a = 1$. The scaling of the *b*-axis Coriolis matrix elements goes as $\sqrt{J(J+1)-K(K+1)}$, which results in strongly *J*-dependent mixing between basis states differing in both K_a and the vibrational quantum numbers. This strong *J*-dependence also leads to states with anomalous effective rotational structure. Because the higher K_a sublevels of $2^13^14^16^1$ can mix with the nominal $2^13^16^2$ $K_a = 1$ level, these are likely candidates for the sources of b_g character, which is shown here to be essential to the interaction with the nearby T_3 level.

Conclusions

SEELEM/LIF spectra of two related bands in the $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ system of acetylene have been recorded to elucidate the nature of S_1-T_3 interaction in acetylene. A simple model is proposed that explains the intensity effects and features in the contrasting SEELEM spectra in the region of the $2^13^16^2$ and $2^13^14^2$ vibrational levels. The $2^13^16^2$ $K_a = 1$ and $2^13^14^2$ $K_a = 1$ vibrational levels are strongly mixed by anharmonic Darling−Dennison interactions. The major difference between these two S_1 vibrational levels is the significant amount of b_g vibrational character mixed into $2^13^14^2$ by *a*-axis Coriolis coupling. This gives rise to enhanced S_1-T_3 mixing in the nominal $2^13^14^2$ level, as observed. When examined together, both the SEELEM/LIF experiment and polyad theoretical arguments add important new details about the nature of the doorway mediated mechanism for intersystem crossing in acetylene.

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