

From Selective to Non-Selective Vibrational Predissociation in Glyoxal van der Waals Complexes

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Vibrational predissociation (VP) of glyoxal complexes formed in a supersonic expansion, has been studied in several vibrational levels of the first excited singlet electronic state $S_1(^1A_u)$ of glyoxal. Light complexes as H_2 -glyoxal display a nice state to state dissociation. Whereas the analysis of the fluorescence spectrum, together with lifetime measurements, have shown that VP is in competition with other intramolecular vibrational energy redistribution processes in these systems, as well as inter-system crossing (ISC). Glyoxal-Ar and glyoxal-Kr behave very similarly. In particular, two isomers exist with different dissociation schemes (but similar for the same isomer of Ar or Kr-complex), and Kr does not seem to enhance ISC. Thus selectivity in the dissociation routes has to be understood as a competition between these deactivation channels.

The photodissociation of van der Waals molecules proceeds through the vibrational predissociation of the weaker van der Waals bond. In a diatomic rare gas complex this photodissociation is non-statistical and, among all the accessible levels of the diatomic the dissociation leads only to the highest energetically accessible levels of this diatomic.¹ In a polyatomic complex the question of the selective or non-selective rupture of the van der Waals band is of importance since it connects with the selective infrared photodissociation.² In such experiments the energy is first localized in one highly excited vibrational overtone, then causes the rupture of a weaker bond.

We studied here the complexes of a polyatomic molecule, trans-glyoxal-(CHO—CHO) with H_2 , D_2 and various rare gases.

We observed two opposite behaviors:

1) The selective, mode to mode dissociation of H_2 , D_2 complexes for which dissociation we give a propensity rule.

2) The near random dissociation of heavy (Ar, Kr . . . glyoxal) complexes where the randomization can be explained in terms of vibrational redistribution within the complex.

EXPERIMENTAL METHOD

The photodissociation is observed in the first excited state 1A_u of the complex and the molecule. The electronic and vibrational states of the complex are very similar to those of the molecule (with in addition the van der Waals modes) as the distant rare gas only slightly perturbs the polyatomic.

The complexes are formed in the supersonic expansion of helium + rare gas (a few %) + glyoxal. The initial (complex) and product species are analyzed through their excitation and their temporally resolved fluorescence spectra.

Glyoxal- H_2 complexes

As an example we show in Figure 1 an energy resolved fluorescence excitation spectrum of H_2 -glyoxal and D_2 -glyoxal in the vicinity of the 8_0^1 transition. Five distinct bands (a, b, c, d and e) clearly belong to a van der Waals mode progressions as evidenced from the H_2 , D_2 isotope effect, band b being the van der Waals origin.

In the fluorescence excitation spectrum, each vibronic transition of the free glyoxal molecule is accompanied by satellite bands assigned to the glyoxal- $(H_2)_1$ complex (all these features are absent in pure He expansion at the same conditions and their pressure dependance ascertains they correspond to a glyoxal- $(H_2)_1$ complex. However, no additional bands could be seen corresponding to glyoxal- $(H_2)_2$ or glyoxal- $(H_2)_3$). The spectral intervals between a reference line of the absorption band of the free glyoxal and its van der Waals features are identical (within $\pm 1 \text{ cm}^{-1}$) for all the vibronic transitions, which implies that the vibrational frequencies of glyoxal are practically non-affected by complex formation. Moreover, no bands corresponding to the rotational excitation of the H_2 component ($J'' = 0 \rightarrow J' = 2$ or $J' = 1 - J' = 3$) have been detected.

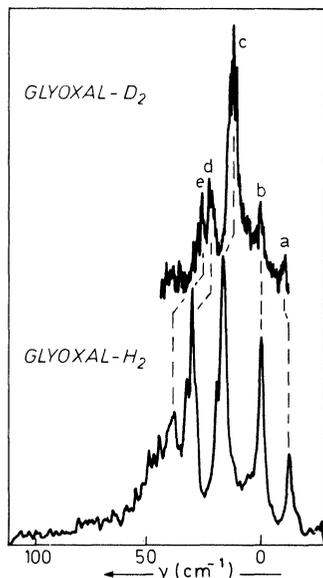


FIGURE 1 State selected (0_0^0 emission of glyoxal fragments) fluorescence excitation spectra of glyoxal- D_2 (upper trace) and glyoxal- H_2 (lower trace) following excitation in the region of the 8_0^0 band of glyoxal. Glyoxal was expanded in a mixture of 5% D_2 or H_2 in Helium at 15 atm through a 32μ nozzle. The peaks a, b, c, d, e are attributed to the same vibrational bands for both complexes, glyoxal- H_2 and glyoxal- D_2 .

We have now examined the dissociation scheme and made first the following observations.

We have observed that for all vibrational levels under study: (i) the vibrational relaxation of free glyoxal molecules is negligible in our experimental conditions; (ii) the excited van der Waals complex dissociates in a much shorter time scale than the lifetime of the glyoxal 1A_u state ($0.8\text{--}2 \mu\text{s}$)³ and than the collision time interval—from fluorescence decay measurements, an upper limit of the order of 15 ns may be established for the dissociation time; (iii) the vibrational dissociation populates lower vibronic levels of the free molecule, the population distribution being identical for all the van der Waals satellites of a given vibronic transition, except for the $\bar{5}_0^1$ transition for which the distribution ratio $7^1/0^0$ has a maximum for feature c. For the $\bar{8}_0^1\bar{7}_0^2$ transition, the resolution was too low to check this assumption.

From the intensity distributions in the fluorescence spectra recorded under the excitation of a given vibronic state of the complex (labelled as $\bar{X}^m\bar{Y}^n$), the branching ratios for different dissociation channels populating the free molecule states $V^k W^1$ may be roughly estimated. They are given in Figure 2 (for the $\bar{5}_0^1$ and $\bar{8}_0^1\bar{7}_0^2$ transitions, we give the average distribution over the five features). Since the $\bar{7}^2$ to 7^1

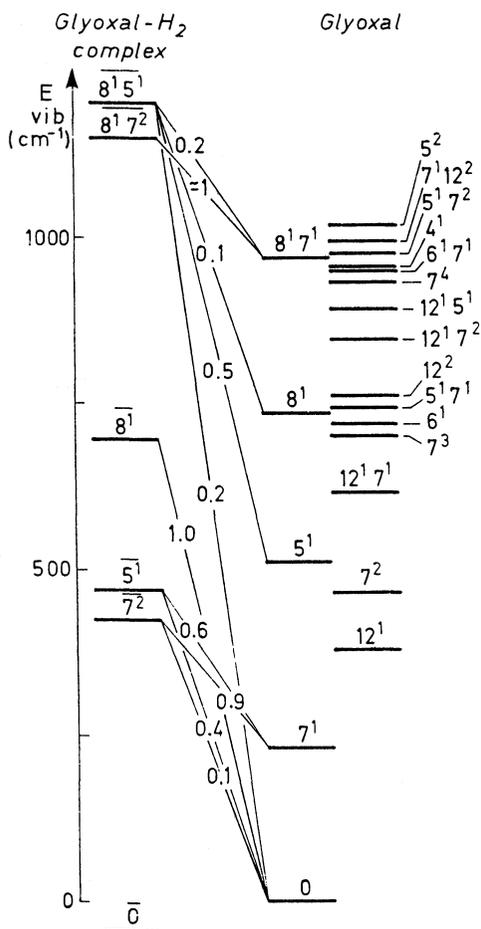


FIGURE 2 Vibrational predissociation pathways of selected complex levels $X_m Y_n$ onto free glyoxal 1A_u fluorescent levels $X^m Y^m$. The relative population ratios are indicated by the middle figures.

process is highly efficient, the dissociation energy of the complex cannot exceed 230 cm^{-1} . As can be seen from Figure 2, most of the energetically accessible states are not populated at all: as in the case of tetrazine,^{4,5} vibrational predissociation in glyoxal is a highly selective process.

Interesting conclusions may be drawn from the behavior of combination states: $\bar{8}^1\bar{5}^1$ and $\bar{8}^1\bar{7}^2$. For the former, the predominant channels are $\bar{8}^1\bar{5}^1 \rightarrow 5^1$ and $\bar{8}^1\bar{5}^1 \rightarrow 8^17^1$, while for the single mode states we have: $\bar{8}^1 \rightarrow 0^0$ and $\bar{5}^1 \rightarrow 7^1$. One can consider that the dissociation takes place by the individual energy transfer either from the 8 or the 5 mode to the dissociation continuum, both processes having similar rates. This is what we could call the "spectator model," mode 8 remaining a spectator while mode 5 dissociates to the continuum and vice-versa. There is, however, a non negligible $\bar{8}^1\bar{5}^1 \rightarrow 0^0$ channel that cannot be understood this way. The spectator model is further verified by the dissociation of $\bar{8}^1\bar{7}^2$ which gives fragments in the 8^17^1 state mainly (the other levels are uncertain and poorly filled), while $\bar{7}^2$ gives 7^1 . The dissociation of the $\bar{8}^1\bar{7}^2$ state would thus consist in the transfer to the continuum of one quantum of the 7 mode, much more efficient than the transfer of one 8 quantum.

The high efficiency of $\bar{7}^2$ to 7^1 process ($\Delta E = 233 \text{ cm}^{-1}$) is consistent with the energy gap law. On the other hand, the energy gap law will predict that level $\bar{5}^1$ should predissociate faster than $\bar{8}^1$ ($\Delta E = 509$ and 735 cm^{-1} respectively) and this is in disagreement with what we see. One possible explanation of this behavior comes from the analysis of normal modes in glyoxal. If we suppose that the H_2 molecule is bound on the C_2 axis out of the plane of glyoxal,⁶ then the van der Waals stretch vibration will be more efficiently coupled to the out of plane vibrations (8 and 7) than to the in-plane vibrations like mode 5, allowing an efficient energy transfer between intra and inter-molecular modes.

These observations can be rationalized when one observes that the connected channels involve only a 1 or 2 quantum change (seldom 3).

Dissociation of argon, krypton-glyoxal complexes

The heavier rare gases are more polarizable hence they complex more tightly to glyoxal.⁹ Moreover we have shown the existence of multiple potential wells, i.e., the formation of two van der Waals conformers,

which we shall call C and C' . From the fluorescence spectra of the dissociated species we have bracketed the dissociation energies:

$$\begin{aligned} 233 \text{ cm}^{-1} < DC(\text{Ar}) < 466 \text{ cm}^{-1} & \quad DC'(\text{Ar}) < 240 \text{ cm}^{-1} \\ 466 \text{ cm}^{-1} < DC(\text{Kr}) < 735 \text{ cm}^{-1} & \quad DC'(\text{Kr}) \approx 250 \text{ cm}^{-1} \end{aligned}$$

We have observed that, aside from the vibrational predissociation there are two competing non-radiative deactivation channels for the complex. The resonant emission observed from the $\bar{0}^0$ complexes in the ${}^1\bar{A}_u$ electronic state is much shorter (110 ns for Kr, 140 ns for Ar) than the $2 \mu\text{s}$ glyoxal emission. We have shown⁷ that this 0^0 deactivation proceeds through intersystem crossing (dissociation into the

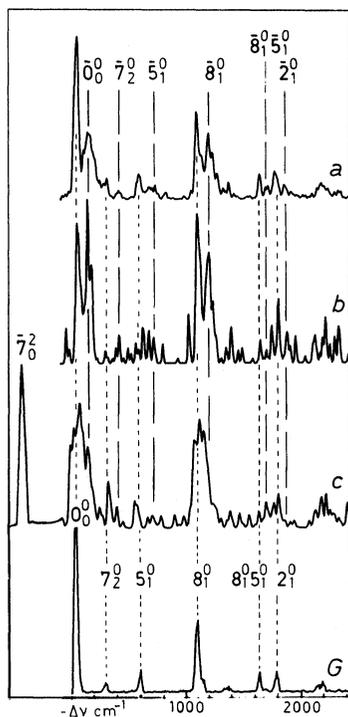


FIGURE 3 Fluorescence emission from the complexes: (a) resonance 0^0 emission of C (Kr), (b) resonance 0^0 emission of C (Ar), (c) emission resulting from 7^2 excitation of C (Kr). The left peak corresponds to the reference scattered laser light, (d) reference glyoxal 0^0 emission.

triplet manifold of glyoxal). When the complexes are excited below the dissociation limit, with some vibrational excess energy, the resonant emission is no longer observed as seen in Figure 3. Here the $\bar{7}^2$ complex of krypton was excited, the sharp structure of resonant emission (as seen for $\bar{0}^0$) does not appear starting from the excitation energy, but a broad emission is formed in the $\bar{0}^0$ emission range. This behavior is characteristic of vibrational energy randomization where the $\bar{7}^2$ level is perturbed by the high density of the $\bar{0}^0$ low frequency (*c.* 30 cm^{-1}) van der Waals modes. This was further confirmed by the decay characteristic of this $\bar{7}^2$ level, very similar (110 ns) to the $\bar{0}^0$ decay. The onset of such randomization is rapid and proceeds within the laser pulse, much faster than intersystem crossing, as must be occurring in the Ar-tetrazine complex.⁸

Selective dissociation occurs when one (or a few) among the dissociation pathways is faster than the others and than randomization. The dissociation is not as selective as for H_2 -complexes (Figures 4 and 5). However in a narrow energy range, some discrimination in the routes is retained and level 12^1 has not been seen in any dissociation channel,

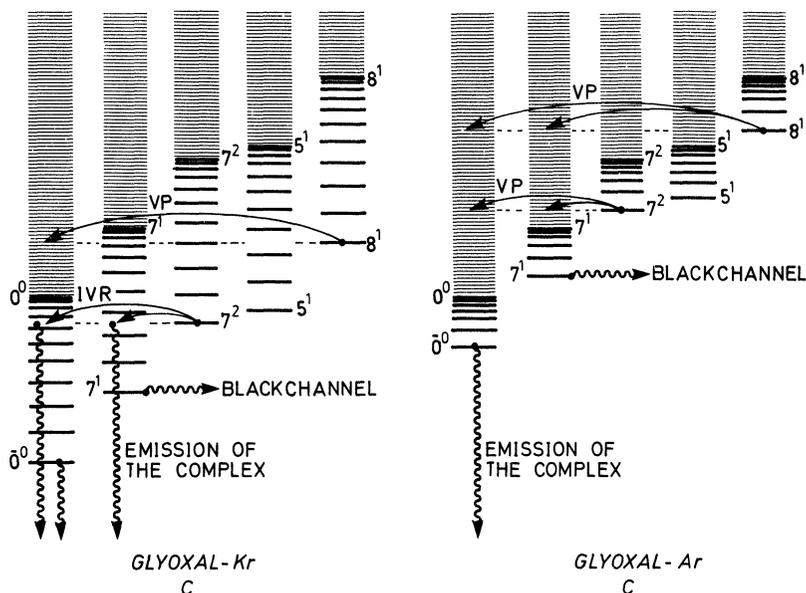


FIGURE 4 Dissociation pathways of C (Argon), C (Krypton) complexes.

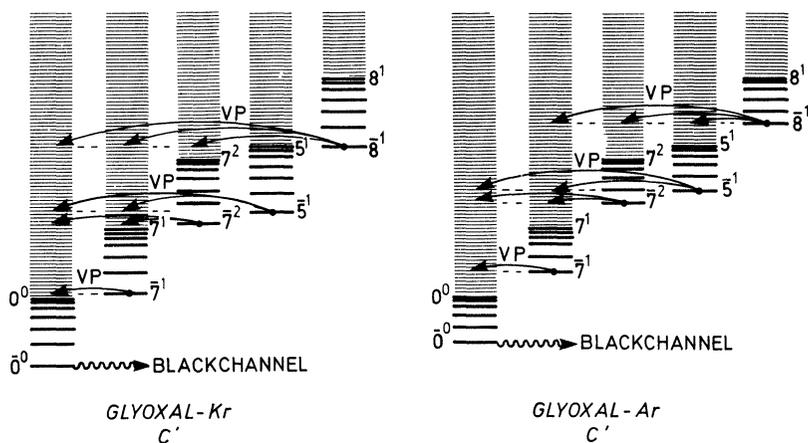


FIGURE 5 Dissociation pathways of C' (Argon), C' (Krypton) complexes.

although it could have appeared in some of them ($E_{\text{vib}} = 380 \text{ cm}^{-1}$).

Symmetry considerations must be important to determine the dissociation pathways as argon and krypton complexes display mostly the same routes. Moreover an identical dissociation scheme is observed in the selective domain of C' - and H_2 -complexes, involving mostly the out of plane torsional mode 7 (symmetry species a_u , $E_{\text{vib}} = 233 \text{ cm}^{-1}$).

CONCLUSION

Vibrational energy randomization is here an important factor of non selectivity in the dissociation routes if not the only one. We wish in the next future, to evidence this further by the picosecond study of the dissociation dynamics.

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