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DISSOCIATION IN SMALL MOLECULES*

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The study of molecular dissociation processes is one of the most interesting areas of modern spectroscopy owing to the challenges presented by even the simplest of diatomic molecules. This paper reviews the commonly used descriptions of molecular dissociation processes for diatomic molecules, the selection rules for predissociation, and a few of the principles to be remembered when one is forced to speculate about dissociation mechanisms in a new molecule. Some of these points will be illustrated by the example of dissociative ionization in O_2 .

Mechanisms for molecular dissociation resulting either from excitation out of the ground state or from the decay of a valence or Rydberg state can be classified as follows [1]:

- (1) Direct dissociation. The most important case of dissociation continua in absorption is that in which a transition occurs from a stable lower state to a repulsive upper state or to the continuous portion of a stable upper state. The energy dependence of the continuum intensity is governed (to a first approximation) by the Franck-Condon principle, i.e., the most probable transition in absorption is that going vertically upward from the minimum of the lower potential energy curve.
- (2) Radiative decay. Molecular dissociation results when a molecule in a stable excited state radiatively decays to a lower repulsive state. This is a common phenomena and the resulting continuous radiation is often used for laboratory light sources.
- (3) Nonradiative decay. When a discrete level overlaps an energetically available dissociation continuum, the possibility exists that the state will decay without the emission of radiation. Such a state normally has a very short lifetime (much shorter than typical radiative lifetimes), and, as a result, the discrete level may appear broadened in absorption. Furthermore, there may be an absence or weakening of molecular emission, since only those molecules that do not decompose may radiate. This process, which is termed predissociation, occurs in diatomic molecules by the conversion of electronic or rotational energy and in polyatomic molecules by these mechanisms as well as the conversion of vibrational energy. Another nonradiative decay process which is analogous to predissociation and which is important in the dissociative ionization process in O_2 and other molecules is preionization. In this process, a discrete level overlaps an energetically available ionization continuum and decays via the

ejection of an electron. The resulting parent ion may then predissociate to form a fragment ion.

Predissociation and preionization are special cases of perturbations, and therefore the same selection rules hold as for perturbations. For diatomic molecules in any coupling scheme [1], $\Delta J = 0, +, -$, and $s \leftrightarrow a$; in Hund's case (a) and (b), $\Delta S = 0$ and $\Delta \Lambda = 0, \pm 1$. If both states belong to case (a), $\Delta \Sigma = 0$; if both states belong to case (b), $\Delta K = 0$; and if both states belong to case (c), $\Delta \Omega = 0, \pm 1$ (rather than $\Delta S = 0$ and $\Delta \Lambda = 0, \pm 1$). Similar considerations apply to preionization; however the quantum numbers and symmetry properties in the continuous range of energy levels now refer to the system of molecular ion plus electron.

The selection rules for predissociation and preionization of triatomic and larger polyatomic molecules may be considerably more complex as the result of the interaction of electronic and vibrational angular momenta. GELBART [2] has discussed the photodissociation of polyatomic molecules in detail in a recent review article as has OKABE [3] in a recent book.

In addition to the energy, symmetry, and angular momentum restrictions imposed on predissociation and preionization processes, the Franck-Condon overlap of the potential energy curves of the interacting states imposes a further constraint that determines which of the allowed predissociations and preionizations will actually occur. It must be remembered that the Franck-Condon principle governs radiationless as well as radiative transitions. In general, a transition is possible if the relevant potential energy curves intersect or at least approach one another closely.

Some of the preceding principles are illustrated using the example of photon-induced dissociative ionization in O_2 [4]. The threshold for O^+ production from O_2 occurs at 17.272 eV and corresponds to the ion pair formation process $O_2 + h\nu \rightarrow O^+ + O^-$. The cross section for this process is highly structured and the ratio of O^+ to O_2^+ is $\approx 1\%$ on the maxima of the peaks. Fig.1 gives a potential energy diagram for states of O_2 and O_2^+ [4_2] and it can be seen that molecular Rydberg states converging to the $b^1\Sigma_g^+$ state of O_2^+ will lie in the region of ion pair formation and are probably responsible for the structure in the ion pair cross section. The correlation of structure in the cross sections for ion pair formation and for parent ion formation is poor and the exact mechanism for this process is not known.

The threshold for O^+ production from O_2 via the dissociative ionization process $O_2 + h\nu \rightarrow O^+ + O + e$ occurs at 18.734 eV. The cross section for this process is also highly structured near threshold; however, the structure now appears on a more intense direct ionization continuum which rises to a maximum at approximately 640 Å and then declines and reaches an almost constant value in the wavelength region of the vibrational convergence limits of the $O_2^+ B^2\Sigma_g^-$ state. The relative photoionization cross sections for O^+ and O_2^+ formation are shown in the region near threshold in Fig.2. The ratio of O^+ to O_2^+ at 640 Å is $\approx 3\%$.

Appreciable direct dissociation may occur by excitation from the ground state of O_2 to the repulsive wall of $O_2^+ A^2\Pi_u$. Both theoretical [6] and experimental [7] Franck-Condon factors show that the $O_2 X^3\Sigma_g^-, v'' = 0 \rightarrow O_2^+ A^2\Pi_u, v'$ transition has a long vibrational progression and that transitions to higher vibrational states ($v' > 15$) occur with approximately 20% of the intensity of the most probable transition. It is probable that direct

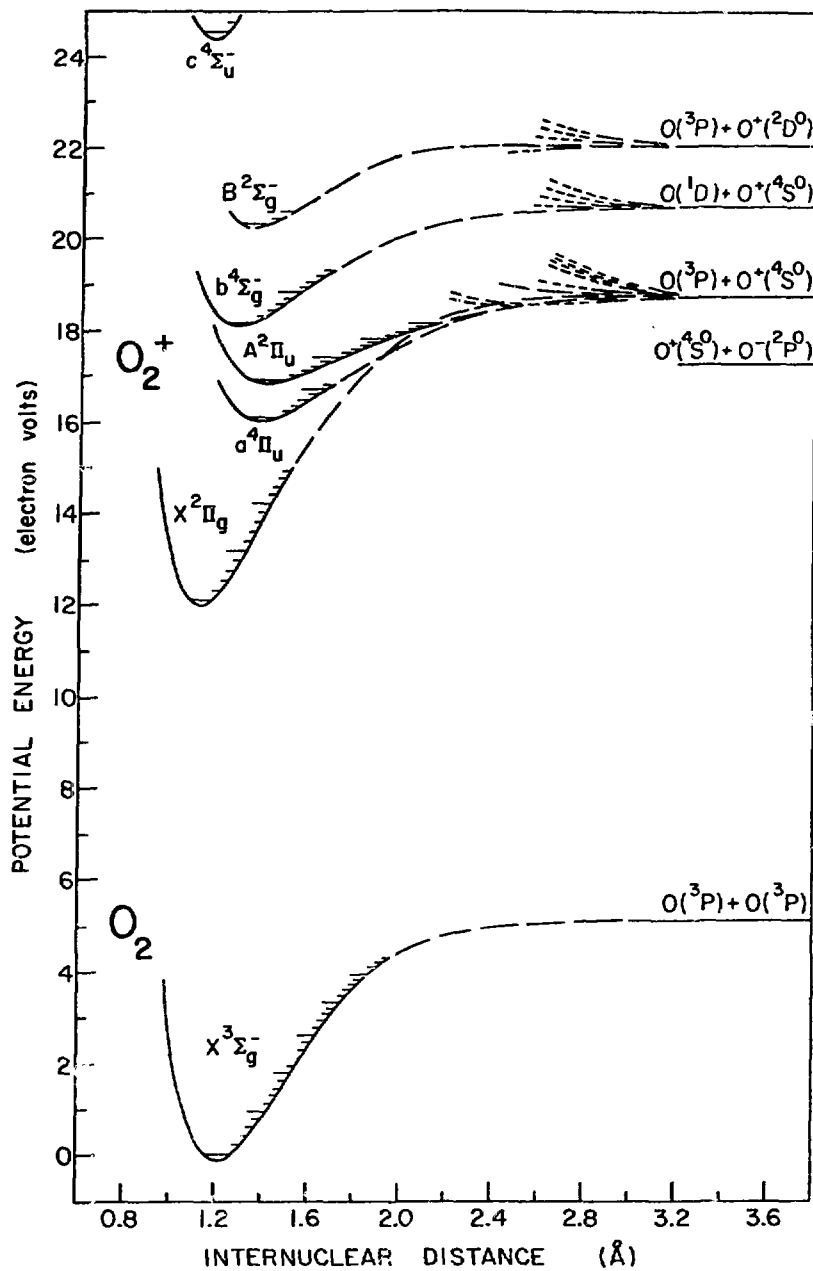


Fig.1 Potential energy curves for the ground state of O₂ and the lower-lying states of O₂⁺, taken from the compilation of GILMORE [5]

transitions to the dissociation continuum also occur with significant intensity and account for the rising continuum near threshold. FREUND [8] has pointed out that this is the most likely mechanism for the production of near-zero kinetic energy O⁺ ions observed in experiments measuring the kinetic energy distribution of O⁺ from dissociative ionization in O₂. The amount of dissociation due to direct ionization will decrease (as does the total ionization cross section) with increasing energy above threshold and together with decreasing collection efficiency accounts for the decline in

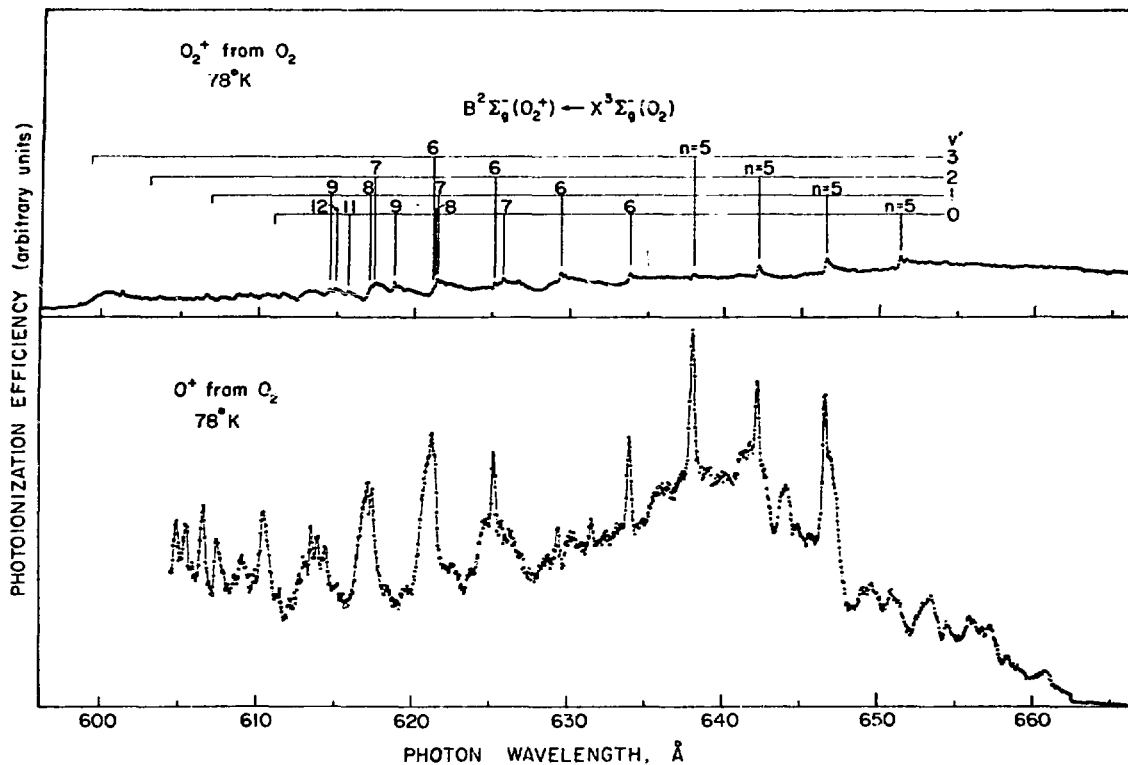


Fig.2 Relative photoionization cross sections for O⁺ and O₂⁺ from O₂ in the region of the threshold for dissociative ionization [4]

cross section above 640 Å. The increase in continuum intensity below about 610 Å probably is due to predissociation of O₂⁺ formed in the B²Σ_g⁻ state by direct ionization.

The peaks in the O⁺ photoionization cross section correspond to Rydberg states in O₂ converging to the B²Σ_g⁻ state of O₂⁺. This structure is not reflected in the O⁺ photoionization cross section and therefore cannot be due to predissociation of the molecular Rydberg states by ion pair states. Rydberg states converging to O₂⁺ B²Σ_g⁻, v = 0 appear very weak in the O⁺ spectrum. The only exception is the n = 6, v = 0 peak; however, this peak occurs at the expected energy of the n = 5, v = 4 state and therefore may not be due to a v = 0 transition. A plausible mechanism for O⁺ production that is suggested by these observations is preionization of the Rydberg states to O₂⁺ b⁴Σ_g⁻, v > 4 followed by predissociation to O(³P) + O⁺(⁴S⁰). The Rydberg states in question have approximately the same potential energy curve as the O₂⁺ B²Σ_g⁻ state to which they converge. The Franck-Condon overlap between O₂⁺ b⁴Σ_g⁻, v > 4 and the various vibrational states of O₂⁺ B²Σ_g⁻ is poor for v = 0 but much improved for v = 1-4 [4]. This would explain the low intensity of the Rydberg states converging to O₂⁺ B²Σ_g⁻, v = 0 in the O⁺ photoionization cross section. Selection rules prohibit predissociation of the b⁴Σ_g⁻ state of O₂⁺ by the A²Π_u or a⁴Π_u states. Predissociation by the ground X²Π_g state of O₂ is allowed but the crossing seems to be very poor; however, only a very small fraction of the

states actually predissociate as is evidenced by the ratio of the O_2^+ to the O_2^+ ion intensities and by the observation of emission from the $b^4\Sigma_g^-$ state of O_2^+ [9].

At higher energies ($E > 20$ eV), quantitative information on the dissociative photoionization process in O_2 can be obtained from the determination of fast electron differential scattering cross sections at negligibly small momentum transfers [10]. Relative optical oscillator strengths are obtained by kinematic correction of the electron scattering intensities according to the Bethe-Born theory. The photoabsorption cross section is obtained from the forward scattered electron energy loss spectrum; the photoelectron spectrum and the photoionization mass spectrum are simulated by the detection of fast scattered electrons in coincidence with ejected electrons ($e, 2e$) and with ejected ions ($e, e + \text{ion}$), respectively.

BRION et al. [10] have used these "pseudo-photon" techniques to study the photoabsorption cross section of O_2 to 300 eV incident energy and the photoionization cross sections to 75 eV incident energy. They found that the cross section for O_2^+ formation increases abruptly at approximately 20 eV and shows a more gradual increase thereafter. The ratio of O_2^+ to O_2^+ is 0.08 at 20 eV, 0.60 at 50 eV, and 0.91 at 75 eV. The reason for this increase in O_2^+ formation is that the $B^2\Sigma_g^-$ state of O_2 , which lies 20.3 eV above the ground state, is completely predissociated as are most of the higher lying ionic states [10]. Therefore, it is not surprising that the increase in total optical oscillator strength above 20 eV (i.e. the oscillator strength due to transitions to the $B^2\Sigma_g^-$ and higher lying excited ionic states) closely parallels the total O_2^+ production.

The preceding example of dissociation in O_2 is among the simplest imaginable. The final (decomposing) states are well defined, the molecule undergoes no collisions with other molecules or surfaces, information on the decay process is available from many types of experiments, and, in many cases, potential energy curves are well known. In contrast, dissociation processes in larger molecules may appear much more complex. However, the basic principles remain the same. The dissociation process will be governed by energetics, angular momentum and symmetry selection rules, the Franck-Condon principle, and competition from other decay channels.

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