Jahn–Teller Effects in the Photodissociation of Ozone[†]

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Abstract: The electronic structure of ozone is examined from the viewpoint of the full 3-fold permutational symmetry of the molecule. The three equivalent wells on the ground electronic state potential energy surface are characteristic of a strong second-order Jahn–Teller effect. It is observed that the ground state and the excited electronic state responsible for photodissociation in the Hartley band ($^1A_1$ and $^1B_2$, respectively, in C_{2v}) are partners in an $^1E'$ representation in the D_{3h} molecular symmetry group and are predicted to exhibit a conical intersection at equilateral geometries. Thus, the photoexcitation of ozone in the region 200 to 320 nm may be viewed as a transition from the lower to the upper branch of a Jahn–Teller system. The implications for the dynamics of ozone photodissociation are discussed.

I. Introduction

From spectroscopic data, ozone in its ground electronic state is known to have an isosceles triangle geometry, with a central angle of 116° 47′. This geometry presents an apparent paradox. All three oxygen atoms are equivalent and indistinguishable (barring isotope effects), yet one of the three is singled out as the central atom. The resolution of this paradox and the recovery of the full 3-fold permutational symmetry of the molecule were first discussed in detail by Berry[1] and have been addressed since by several other authors.[2] The resolution involves the existence of three identical minima on the ground electronic state potential energy surface, corresponding to each of the three oxygen atoms occupying the central position. These three "isomers" of ozone may interact with each other by tunnelling, but the time scale for this process in the ground vibronic state, estimated at 10^{90} s[1], is so long that each form can be considered independently for most purposes.

There are, however, situations where the full 3-fold symmetry is indeed important. One case involves highly excited vibrational states of ozone in its ground electronic state, where there is no reason to expect tunnelling contributions to be negligible. Such highly excited vibrational levels can in principle be prepared by direct overtone excitation, multiphoton absorption, or emission from an excited electronic state. A second case involves the excitation to an excited electronic state in which there are no barriers between the different forms of ozone, or in which the barriers are surmountable on chemically significant time scales. Such a situation will be in force in photodissociation of ozone in the Hartley band. In this case interference effects, arising from the different initial forms, are in principle observable. The latter case provides the main motivation for this article.

The present situation provides an example of a molecule that undergoes large amplitude motion. Such molecules, generally termed "floppy", cannot be treated within the framework of conventional point group symmetry. The correct framework for discussing symmetry of floppy molecules was introduced by Longuet-Higgins,[3] and involves the larger permutation–inversion (PI) group of the molecule, a subgroup of which is isomorphic to the point group. The description of vibronic transitions within this larger group involves the following program:[4] (1) relabeling of the electronic states with labels appropriate to the PI group; (2) relabeling of the rovibrational states within the PI group; (3) assignment of a symmetry label to the transition dipole moment within the PI group; and (4) evaluation of allowed transitions to specific rovibronic final states, also labeled within the PI group. There is a fifth step, for excitation to a dissociative electronic state:[5] (5) correlation of the united molecule PI symmetry label with symmetry labels of the fragments.

The new results that emerge from this expanded symmetry treatment may be classified as being of two types, static (electronic) and dynamic (rovibronic). The reassignment of the electronic structure is the subject of section II and yields the following result. The ground electronic state and the excited electronic state responsible for photodissociation in the Hartley band ($^1A_1$ and $^1B_2$, respectively, in C_{2v}) are partners in an $^1E'$ representation in the PI group. There are several intriguing implications of this reassignment: the ground electronic state of ozone, with its three equivalent potential minina, is a classical example of the much sought strong second-order Jahn–Teller effect; the ground and excited state are predicted to exhibit a conical intersection at equilateral geometries; and the photoexcitation of ozone in the Hartley band, which is responsible for the absorption of most of the solar radiation in the range 200 to 320 nm, is a transition from the lower to the upper branch of a Jahn–Teller system.

In section III dynamic effects are discussed. The rovibrational states are relabeled, and several interesting implications for the photoabsorption and final products distributions are considered.

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(2) Kellman, M. *J. Phys. Chem.* **1983**, *87*, 2161.
(3) Longuet-Higgins, H. C. *Mol. Phys.* **1963**, *6*, 445.
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Table I. Resolution of Species of Point Group D_{3h} into Those of C_{2v}

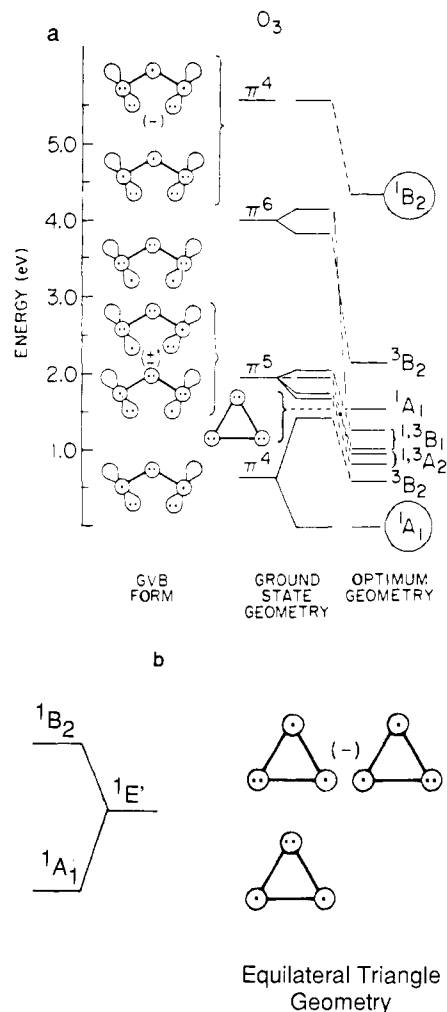| D_{3h}	$C_{2v}(\sigma_h \rightarrow \sigma_v(yz))$	S_3	S_2
A_1'	A_1	A_1	A
A_1''	A_2		
A_2'	B_2	A_2	B
A_2''	B_1		
E'	$A_1 + B_2$	E	$A + B$
E''	$A_2 + B_1$		

The 3-fold permutational symmetry may be the source of the anomalous vibronic structure atop the Hartley absorption continuum.[6] It does not, however, appear to play a role in the anomalous odd/even rotational distribution of the nascent $O_2(^1\Delta_g)$ fragment.[7,8] Full dynamical calculations within this framework will be presented in a separate publication.

II. Reexamination of the Electronic Structure of Ozone from the Perspective of D_{3h} Symmetry

The electronic states of O_3 have been the subject of numerous theoretical studies[9–19] and several studies of the ground-state potential energy surface have been carried out.[11,19] The ground (X^1A_1) state of O_3, with an equilibrium geometry of $R = 1.271$ Å and $\theta = 116° 47'$, dissociates to $O_2(^3\Sigma_g^-)$ and $O(^3P)$. The $^1B_2$ state ($R = 1.405$ Å and $\theta = 108°$ in C_{2v} symmetry) correlates with $O_2(^1\Delta_g) + O(^1D)$ and is dissociative. Both states have $^1A'$ symmetry along the C_s dissociation path. Here we focus on the relabeling of these two states under D_{3h} symmetry, which is isomorphic with the PI group of ozone.

The standard correlation tables, while providing a unique correlation in going from a group of higher symmetry to one of lower symmetry, do not uniquely determine correlations in the other direction.[20] The correlation table between the D_{3h} and C_{2v} point groups is shown in Table I. It is readily seen that A_1 under C_{2v} may correlate with either A_1' or E' under D_{3h}, and B_2 under C_{2v} may correlate with either A_2' or E' under D_{3h}. The correct correlations must be based on an examination of the electronic wave functions and their behavior under adiabatic distortion from C_{2v} to D_{3h}. In some cases, numerical calculations may be necessary to determine this correlation. In the present case, we purport that the correlation can be made by inspection.

Figure 1a shows the GVB form of the low-lying electronic states of O_3. It is important to note that both the ground $(^1A_1)$ and the excited $(^1B_2)$ states are of the π^4 type (four π-electrons perpendicular to the molecular plane). Consider distorting both the ground $(^1A_1)$ and the excited $(^1B_2)$ states to equilateral triangle geometry. Figure 1b illustrates the out-of-plane π-orbital structure of these states at the new geometry. It is clear that neither of these states has 3-fold rotational symmetry; in fact, the $^1A_1$ and $^1B_2$ states are of rotated images of each other at this geometry. This observation suggests that the $^1A_1$ and $^1B_2$ states are degenerate at the equilateral triangle geometry and consequently the

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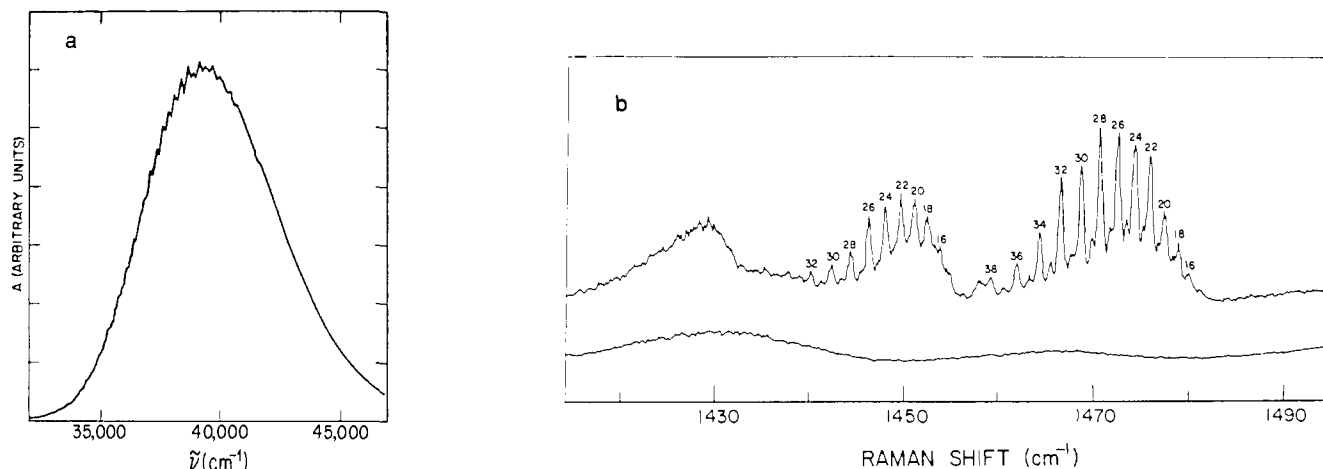(18) Rama Krishna, M. V.; Jordan, K. D. *Chem. Phys.* **1987**, *115*, 423.
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Figure 1. (a) Structure of the low-lying electronic states of ozone under C_{2v} geometry. (Reproduced with permission from ref 9. Copyright 1973 American Chemical Society.) (b) Out-of-plane π-electron structure of the $^1A_1$ (ground) and $^1B_2$ states, adiabatically distorted to the equilateral triangle geometry. Note that the two states are simply rotated images of each other, suggesting that they are partners in a $^1E'$ representation under D_{3h} symmetry.

correct correlation to irreducible representations of D_{3h}, among the possible choices given in the previous paragraph, is that they are partners in an $^1E'$-type representation. This correlation is consistent with the observation that the $^1A_1$ and $^1B_2$ are both singlets.

The degeneracy of the two electronic states is strongly broken away from the equilateral triangle geometry. This is the well-known Jahn–Teller effect, which applies to molecules with 3-fold or higher axes of symmetry in E-type electronic states. The strong distortion away from the fully symmetrical equilateral geometry in the ground electronic state is characteristic of a first-order Jahn–Teller effect.[21,22] The presence of three equivalent wells on the ground-state surface, separated by high barriers (see below), is the signature of strong second-order Jahn–Teller coupling.[21,22] Hence, the photodissociation of ozone in the Hartley band (200–320 nm) may be viewed as a transition from the lower to the upper branch of a conical intersection. Child and Longuet-Higgins discussed this case many years ago.[23] Suffice it to say that the transition may be very strongly electronically allowed for perpendicular polarized light (dipole moment operator transforming as E'). This is the case with ozone.

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Figure 2. (a) Ozone absorption spectrum in the Hartley band. Note the anomalous vibrational structure atop the broad continuum, with a spacing of ~ 250 cm^{-1}. (Reproduced with permission from ref 6. Copyright 1973 American Institute of Physics.) (b) Vibrational and rotational final product distribution of the nascent $O_2(^1\Delta)$ produced in the photodissociation of ozone at 266 nm. Note the anomalous alternation of intensity between even and odd rotational states of $O_2(^1\Delta)$. (Reproduced with permission from ref 7. Copyright 1973 Elsevier, Amsterdam.)

The ab initio potential energy surfaces for ozone calculated in ref 11 and tabulated in ref 19 have been examined for evidence of degeneracy at the equivalent triangle geometry. If the $^1A_1$ and $^1B_2$ states truly correlate with the same $^1E'$ state, the equilateral triangle geometry energies should be degenerate for all perimeters. This feature is in fact *not* observed. The explanation lies in the fact that the calculations of ref 11 were performed at bond angles greater than $110°$ and extrapolated by an analytic fitting function to equilateral geometries, well beyond their range of validity. However, a set of unpublished calculations performed by Pack using a fully symmetrized minimal basis set does indeed indicate the presence of a conical intersection of the $^1A_1$ and $^1B_2$ states at equilateral triangle geometries.[24]

This leads to an important consideration that must be added to the methodology of the development of empirical and semi-empirical potential energy surfaces of molecules with 3-fold (or higher) permutational symmetry.[15,16] The general procedure must take into account the possible existence of a conical intersection at the equilateral geometry; otherwise there are prima facie errors in the surface near this region. Depending on the molecule and the energies involved this could be a serious failing.

The relabeling of the ground and the excited electronic states as E' symmetry has implications for the rovibrational states that exist, in keeping with the Pauli principle. Since O^{16} (nuclear spin 0) is a boson, the full rovibronic $\times$ nuclear spin wave function must transform as $A_1^{+/-}$ (even or odd parity). Only nuclear spin wave functions of species A_1 exist. Since the electronic species has just been relabeled as E', the rovibrational species must transform as E' or E''. There are, however, no restrictions on vibrational levels per se, since rotational states of all symmetry species exist. The vibrational species must, however, be paired with rotational states of the correct symmetry. The vibrational levels and the associated rotational levels that are symmetry allowed are indicated in Table II.

III. Consequences for the Photodissociation Dynamics and the Spectroscopy

The classification of ozone within its full PI group (S_3^*, which is isomorphic with D_{3h}) has several consequences for the photoabsorption and photodissociation dynamics, as will now be discussed. There are two outstanding experimental anomalies connected with ozone photodissociation. The first is a weak, sharp vibronic progression, with a spacing of 250 cm^{-1}, atop the broad Hartley absorption continuum[6] (Figure 2a). The second is an alternation in intensity of even and odd rotational final states in the nascent $O_2(^1\Delta_g)$ photofragment[7,8] (Figure 2b). The original motivation for the relabeling of the rovibrational and electronic

Table II. Vibrational Symmetry Species and the Associated Rotational Species

Γ_v	$\times$	Γ_r	$=$	Γ_{rv}
A_1'		E' (K = 2, 4, 8, 10, ...)		E'
		E'' (K = 1, 5, 7, 11, ...)		E''
A_2'		E' (K = 2, 4, 8, 10, ...)		E'
		E'' (K = 1, 5, 7, 11, ...)		E''
E'		A_1',A_2' (K = 0, 6, 12, ...)		E'
		A_1'',A_2'' (K = 3, 9, 15, ...)		E''

states in D_{3h} symmetry was the hypothesis that the full permutational symmetry was connected with these experimental anomalies.

To gauge the importance of consideration of the 3-fold symmetry of the system, it is instructive to examine the ground and excited potential energy surfaces in a coordinate system which reveals this symmetry. Figure 3a,b shows the ground state and excited state empirically modified potential energy surfaces, after ref 19. The potentials are plotted in q_2 vs q_3, which are asymmetric stretch and bend symmetrized bond length coordinates. Note that the ground-state surface has three identical minima, corresponding to each of the three O atoms occupying the central position in the molecule. The excited state has three identical saddle points very near the three ground-state equilibrium geometries, reflecting the fact that it is unstable in the asymmetric stretch coordinate. Between the three saddle points lie three equivalent exit channels, corresponding to the three asymptotic arrangements of $O + O_2$ fragments.

Circular motion in the q_2–q_3 plane is often called pseudorotation and corresponds to a cyclical interchange of pairings among the three O atoms. The presence of the three distinct arrangement channels will have observable consequences if classical trajectories, or more precisely, the time-dependent quantum mechanical states, execute at least one-third of a pseudorotation. In this case quantum mechanical interferences between the different initial configurations become possible. This dynamical pseudorotation is, in fact, observed in about 10% of the excited-state trajectories,[19] *manifesting itself as an exit of the central O atom*, suggesting that the 3-fold symmetry will have observable consequences.

Our findings relative to each of these two experimental anomalies are now discussed.

a. Photoabsorption Spectrum. The ground vibrational state of the ground electronic state is properly a linear combination of three lobes, one located in each of the ground surface minima. The three lobes give rise to an A_1' and an E' pair of vibrational levels. The splitting between these vibrational levels is infinitesimal for our purpose and leads to a clustering, or induced 3-fold degeneracy. All of these vibrational levels are consistent with the Pauli principle, as discussed above, when paired with rotational

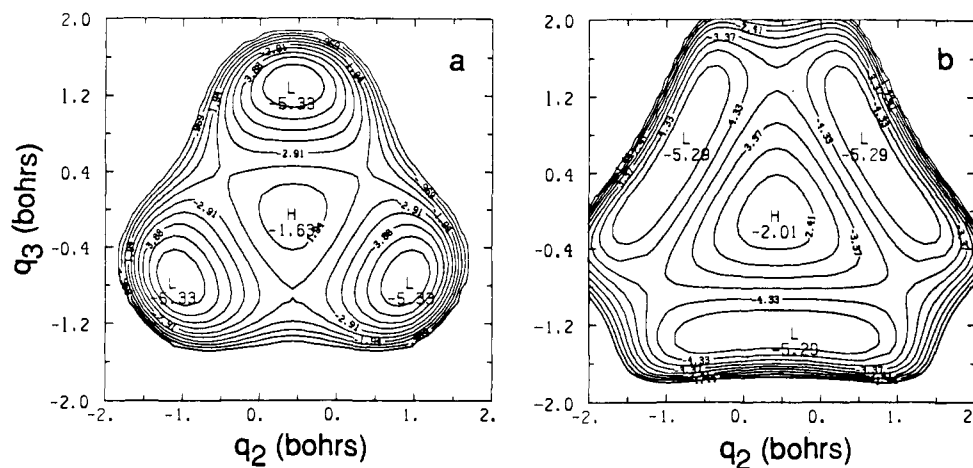(24) Pack, R. T., private communication.

Figure 3. Plot of the ground (a) and excited state (b) potential energy surfaces, following the empirically modified surfaces of ref 19. The potentials are plotted in q_2 vs q_3, which are an asymmetric stretch and a bend coordinate, in order to illustrate the 3-fold permutational symmetry of the system. Note that the ground-state surface has three identical minima, corresponding to each of the three O atoms occupying the central position in the molecule. The excited state has three identical saddle points very near the three ground state equilibrium geometries, reflecting the fact that it is unstable in the asymmetric stretch coordinate. Between the three saddle points lie three equivalent exit channels, corresponding to the three identical arrangements of O + O_2 fragments.
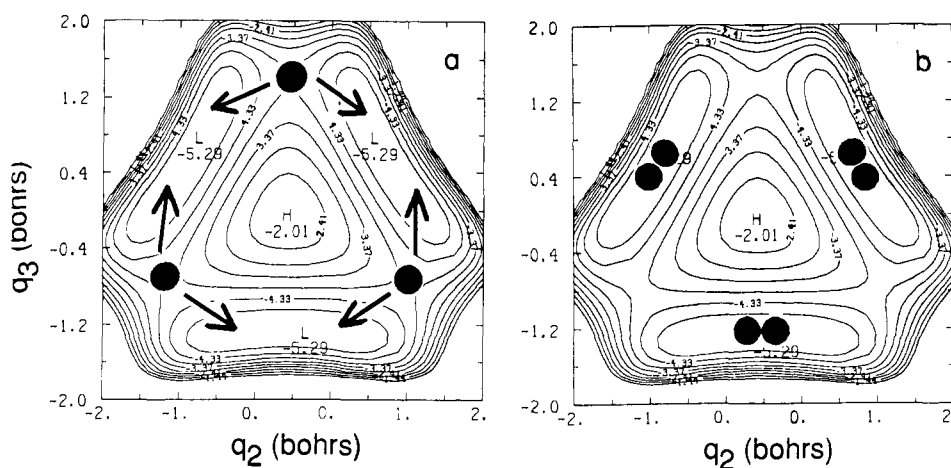

Figure 4. (a) The three lobes of the initial wave packet in a totally symmetric (A_1) linear combination, superimposed on the excited state surface. Each of the three wave packets will bifurcate, and amplitude from neighboring wave packets will *confluesce* into each of the three exit channels, shown schematically in part b. Note the even symmetry of the lobes in the fragment region, indicating that only *even* rotational fragment states will be produced. (This correlation, strictly speaking, applies to A_1 *rovibrational* states of the parent.)

states of the correct symmetry. We will consider primarily the A_1' vibrational wave packet where the three lobes all have the same sign.

Figure 4a shows the three lobes of the initial wave packet in the A_1' linear combination, superimposed on the excited-state surface. To most easily understand the consequences of the dynamical permutation on the photoabsorption spectrum, the wave packet formulation of photodissociation and photoabsorption is adopted. In this picture, the initial vibrational state of the ground electronic state executes a vertical transition to the excited electronic state. This nonstationary initial state begins to evolve in time on the excited state potential surface. The photoabsorption spectrum is then given by the Fourier transform of the wave packet autocorrelation function. Vibronic structure in the frequency domain is associated with a wave packet recurrence in the time domain, or crudely speaking, a return of the ozone molecule to its original geometry.

A consequence of the 3-fold symmetry is that a recurrence in the wave packet autocorrelation function can arise from a lobe of the wave packet *not* returning to its initial location, but evolving to one of the neighboring sites. Another way of stating this is that, as a consequence of the permutational symmetry, the molecule need not come back to its original geometry, provided it comes back to a geometry related to the original within a permutation. Presumably, there was no structure in the calculations of ref 11 and 19 because the initial wave packet was not

symmetrized. Calculations repeating the calculations of ref 19 using symmetrized initial states will be presented in a separate publication.

b. Final Product Distributions. Figure 4a, discussed above, shows the $A_1'(+ + +)$ vibrational state at $t = 0$. The amplitude of this state when dissociation is nearly complete is shown schematically in Figure 4b. Note that as each of the three wave packet lobes exits there is actually a *confluence* of wave packet amplitude, arising from amplitude originating in different configurations funneling out of the same exit channel. Further consideration of Figure 4b suggests that there may be selection rules between the symmetry species of the parent O_3 molecule and the rotational states of the O_2 fragment. Specifically, the A_1' state leads to a symmetric arrangement of amplitude in the O + O_2 asymptotic region (Figure 4b) and correlates to *even* rotational states of O_2.

Figure 5a shows a vibrational state of $A_2'(+ + +)$ symmetry at $t = 0$. (Note that this is an *excited* vibrational state of the ground-state surface, corresponding to $v = 1$ in the asymmetric stretch of the C_{2v} molecule. It is included here to complete the symmetry discussion, although its role in the photodissociation process at cold temperatures is negligible.) The amplitude of this state when dissociation is nearly complete is shown schematically in Figure 5b. Note that as each of the three double-lobed wave packets bifurcates there is again a *confluence* of wave packet amplitude; this time the dissociation leads to an antisymmetric arrangement of amplitude in the O + O_2 asymptotic region (Figure
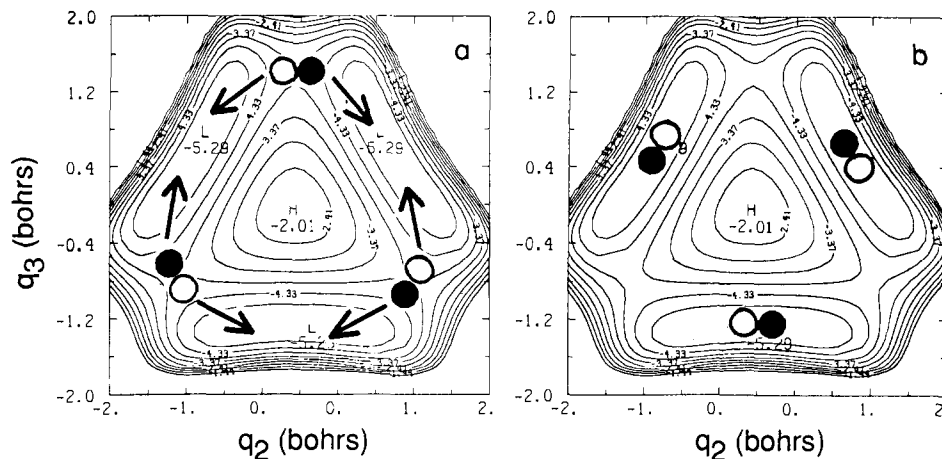
Figure 5. (a) The initial wave packet in an A_2 state, superimposed on the excited state surface. Each of the three wave packets will bifurcate, and amplitude from neighboring wave packets will confluesce into each of the three exit channels, shown in part b. Note the odd symmetry of the lobes in the fragment region, indicating that only *odd* rotational fragment states will be produced. (As above, this correlation is properly applied to the A_2 *ro*vibrational states of the parent.)

5b) and correlates with *odd* rotational levels of O_2.

These rules should properly be applied to the *rovibrational* not simply the vibrational states of the parent and fragment.[5] With this proviso, the correlations may be corroborated rigorously by inspection of Table I. Invoked above to correlate from C_{2v} to D_{3h}, Table I may now be read in the opposite direction to correlate parent states (group S_3) to fragment states (S_2) (the O_2 fragment has 2-fold permutational symmetry). A_1 levels of the parent are seen to correlate with A levels of the O_2 fragments (symmetric under permutation and hence even rotational states); A_2 levels of the parent correlate with B levels of the fragments (antisymmetric under permutation, and hence odd rotational levels); E levels of the parent correlate with both A and B levels of the fragments (even *and* odd rotational states).

As discussed above in connection with the relabeling of the electronic symmetry, only rovibrational states of symmetry species E′ or E″ may exist on the ground state and the excited electronic state. According to the previous paragraph these E rovibrational states may correlate with either even or odd *j* levels of the $O_2(^1\Delta_g)$ fragment,[5] and consequently there are no implications for Valentini's final product studies.[7,8] If however, the excited electronic state had been correlated with $A_2′$ the rovibrational state would be required to be A_2 as well, and only odd *j* levels of the $O_2(^1\Delta_g)$ fragment would be allowed!

Although this treatment yields a negative result with respect to Valentini's results, the correlation of symmetry species of parents and fragments appears to be a very powerful, general method, and may be expected to have widespread consequences for rotational and vibrational final state populations in many other systems. Since the time of his original publication Valentini et al. have published a satisfying explanation of the anomalous alternation of even and odd intensity in terms of a selective depletion of odd rotational levels to the ground ($^3\Sigma_g^-$) state of the O_2 fragment.[8]

IV. Conclusions

The electronic structure of ozone has been reexamined from the viewpoint of the full 3-fold permutational symmetry of the molecule. The three equivalent wells on the ground electronic state potential energy surface are characteristic of a strong second-order Jahn–Teller effect. It is observed that the ground state and the excited electronic state responsible for photodissociation in the Hartley band ($^1A_1$ and $^1B_2$, respectively, in C_{2v}) are partners in an $^1E′$ representation in the D_{3h} molecular symmetry group and are predicted to exhibit a conical intersection at equilateral geometries. Thus, the photoexcitation of ozone in the region 200 to 320 nm may be viewed as a transition from the lower to the upper branch of a Jahn–Teller system.

The full 3-fold permutational symmetry of ozone needs to be taken into account in studying the dissociation dynamics. This

involves use of the permutation–inversion group machinery developed by Longuet-Higgins for "floppy" molecules and extended to Quack to chemical reactions and photodissociation. The appropriate group consists of all "feasible" permutations of identical nuclei, where the definition of feasible depends on the energies and dynamics of the process under study. There appears to be a profound relationship between feasible permutations (group theory) and saddle points of the potential energy surface (topology). This connection will be explored in greater detail elsewhere.

The full 3-fold permutational symmetry of ozone may be the source of the anomalous vibronic structure atop the Hartley absorption continuum. This possibility is now being explored, in this and other laboratories,[25] using semiclassical and quantum calculations of the dissociation dynamics. The 3-fold symmetry does not, however, seem to play a role in the unusual alternation between even and odd *j* states of the $O_2(^1\Delta_g)$ fragment produced in the dissociation.

Several other consequences of the specifically Jahn–Teller character of ozone photodissocation are worth noting. The presence of a conical intersection, and at least partial pseudorotation about this singular point, suggests that there may be additional observable effects arising from development of an adiabatic phase.[26-29] This pseudorotation, if fully executed, would entail the accumulation of a phase of π on the nuclear wave function, and experimentally observable interference effects between pseudorotated and nonpseutorotated amplitude in the fragments. If a pseudorotation of only $2\pi/3$ or $4\pi/3$ is executed, the motion would entail exit of what had initially been the central oxygen, which would interfere with nonpseudorotated amplitude originating from a different initial isomer.

The existence of a conical intersection places an additional symmetry constraint on the potential energy surfaces of ozone. It may be desirable to modify the empirical fitting method of MSV[15,16,19] to properly pair the ground and excited surfaces of molecules in ozone and other molecules exhibiting a conical intersection. A good way to proceed along these lines may be to start with the quadratic Jahn–Teller form[21,22,29] in the E′ vibrations and use a general anharmonic form for the A′ and A′–E′ coupling. Modifications of the MSV method to properly include conical intersections, and studies of the role, if any, of Berry's adiabatic phase in the dissociation process, are in progress.

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