

Time-Dependent Measurements and Molecular Structure: Ozone*

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I. GENERAL: STATIONARY STATES AND TIME-DEPENDENT MEASUREMENTS

A. Introduction

MOLECULAR quantum mechanics and molecular spectroscopy have concerned themselves principally with the description of stationary states of molecules and of transitions between these states. One chooses a Hamiltonian operator \mathcal{H} containing the information one has about a system and then derives an approximate solution to the time-independent Schrödinger equation, subject to limitations of machine capacity, approximations in \mathcal{H} , and restrictions on the functional form of the solution.

Let us first consider the restrictions applied to the Hamiltonian. These take a variety of forms. In calculating electronic energy levels, one usually tries to use the Born-Oppenheimer approximation; in this case the system becomes the set of electrons, and the Hamiltonian contains charges, masses, and internuclear distances as fixed parameters. Going one step further, when we calculate energy levels for a vibrating rotor, we no longer fix the actual interparticle vectors, but treat them as operators. We generally do use the small-oscillation approximation, however, so that equilibrium positions appear as parameters in \mathcal{H} and the actual distances are in effect constrained to the vicinity of the equilibrium positions. We cannot always do this alone but must often allow particle statistics to enter; the rotation-vibration energy levels of a homonuclear diatomic can only be determined if we include the quantum statistics of the nuclei. Further still, the hindered rotors like ethane and the inverting umbrellas like ammonia form classes of molecules whose spectra demand that we write certain internuclear coordinates such as the azimuthal angle of C_2H_6 or the nitrogen-to-base-plane distance of NH_3 as true operators. In dealing with molecules like these we continue to treat most internuclear distances in the small-oscillation approximation, but the existence of the tunneling motions of internal rotation and inversion force us to leave the range of certain operators unrestricted.

We proceed to the question of specifying stationary states of a molecule, with particular reference to the kind of approximations associated with restrictions on the Hamiltonian. With this, we must bear in mind the complementary problems of the detection of a molecule in a nonstationary state: when can we expect to observe

a nonstationary state; and what circumstances and molecular properties might be used to distinguish nonstationary and stationary states? Our discussion of these questions generally is stated in terms of the states of a set of nuclei in a molecule, although the same considerations would hold for any quantum mechanical system of several particles. We cite a few examples of molecules to which the argument might apply. In the second major part, we discuss the ozone molecule as one of the very simplest systems for which the viewpoint developed here might be helpful.

B. Criteria for Stationary States

In his discussion of molecular spectra, Hund¹ pointed out that rotation and small-amplitude vibrations would

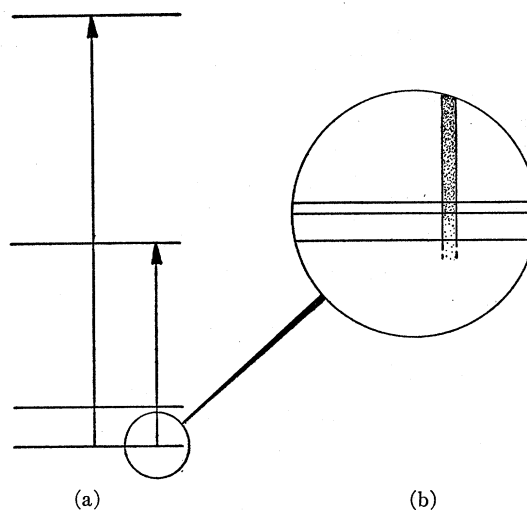


FIG. 1. A schematic diagram of the relation between line width and stationary states.

not always suffice to describe the dynamics of nuclear motion. Molecules having two or more minima on their vibrational potential energy surfaces would, under favorable circumstances, exhibit tunneling, and their spectra could only be interpreted fully if this were taken into account. Hund investigated the relation of nuclear masses to tunneling frequencies and pointed out the equivalence of tunneling frequencies and the splittings of stationary states. The argument is the classical one for the energy-time form of the uncertainty principle, $\Delta E \Delta t \geq \hbar/2$. A fast measurement of some property \mathcal{Q} requires a small interval, Δt , and has a large associated

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¹ F. Hund, *Z. Physik* **43**, 805 (1927).

ΔE ; if ΔE is large compared with the separation of several stationary states, we may observe the value $\langle \mathcal{R} \rangle$ appropriate to mixtures of the stationary states. On the other hand, a slow measurement of \mathcal{R} , requiring a long interval Δt , may have a small associated uncertainty in energy; in this case ΔE may be much less than the separation of stationary states so that $\langle \mathcal{R} \rangle$ is that appropriate to stationary states. These two cases are shown schematically in Fig. 1. On the left, the drawing indicates two transitions between widely separated levels; these might be energy levels of the electrons in a molecule. On the right is indicated a set of levels very closely spaced, such as hyperfine levels in a molecule might be. In the transition shown, the ΔE of the process, indicated by the shaded tail of the arrow, is sufficient to eradicate any significance of the hyperfine levels.

A variety of examples have been discussed in terms of tunneling. The hindered rotor and ammonia inversion problems mentioned previously are well known²⁻⁴; closely allied to the ammonia problem is the inversion of optical isomers.² Still another example is the pseudo-rotation of cyclopentane.⁵

As a starting point, we refer to a discussion given by Wilson⁶ regarding the problem of "catching" an ethane molecule in one of its three potential wells. Wilson pointed out that a molecule in such a state would be in a nonstationary state of a special sort; this nonstationary state can be constructed exactly by superposing the three lowest stationary states, one A_1 and two E , in equal proportions. By using a measuring process or condition such that the ΔE of the process is larger than the splitting of the torsional levels, we can observe the nonstationary state of a molecule "caught" in one well. On the other hand, observation of a stationary state of ethane requires a measurement technique whose photons are fairly monochromatic, and, having only a narrow band of Fourier components, are quite extended in space. Such photons obviously take a relatively long time interval Δt to pass the system in question, so we see again that as low measurement is associated with detection of stationary states. Such slow and high-resolution measurements are especially characteristic of the radio-frequency techniques: microwave, electron spin resonance, nuclear magnetic resonance, and electric quadrupole resonance spectroscopy.

It might be helpful to examine explicitly some criteria regarding the possibility of observing nonstationary states. We could then use methods like those

² G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945).

³ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

⁴ E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955). Also see the material to which references 2-4 refer.

⁵ J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.* **69**, 2483 (1947).

⁶ E. B. Wilson, Jr., *Bull. Am. Phys. Soc. Ser. II*, **4**, 164 (1959).

of Hund¹ or Wilson⁷ to select the circumstances under which such states would be detectable, and then to decide how results of such measurements would differ from stationary state observations. For certainly they must give information not readily accessible from the stationary states alone if nonstationary states are worth explicit characterization. The criteria we seek are related to the information contained in the Hamiltonian and how we deal with this information.

From one viewpoint, the Hamiltonian \mathcal{H} contains just two kinds of information; first, it expresses all the force laws for interactions between the parts of the system, and second, it contains all the data regarding the symmetry of the problem. We are concerned with the treatment of the symmetry and so should see exactly how this information appears in \mathcal{H} . An exact Hamiltonian gives only two kinds of symmetry information, by way of its own invariances; an exact Hamiltonian is invariant to a change of external coordinate system and also to an interchange of two identical particles. The spatial symmetry, as Ramsey has pointed out,⁸ leads directly to the conclusion that in a stationary state the expectation value of a molecular electric dipole moment μ is zero. Only when the molecular state is nonstationary can we measure an electric dipole. We can do this by applying external electric fields so that the molecule is no longer the entire system. The molecule then goes into a nonstationary state composed of a mixture of excited electronic and rotational states, whose superposition allows us to measure μ in a molecule-fixed coordinate system.

It is the particle symmetry rather than the spatial symmetry which we investigate. As the beginning of this discussion indicated, we frequently use our intuitions to decide how to restrict the operators of \mathcal{H} so that a given problem is made easier. At the same time, we destroy the full permutation symmetry of \mathcal{H} . The Born-Oppenheimer approximation is the most stringent kind because it forbids any interchange of nuclei, even by over-all rotation of the molecule. The numerical parameters in \mathcal{H} fix the geometry and therefore the symmetry of the nuclear framework. (We do actually make use of rotational symmetry in this case because it makes problems easier, not harder.) The small-oscillation approximation allows the molecule to rotate so that some interchange of identical particles may be permitted as dynamical motions. The symmetry of \mathcal{H} , however, is dictated again by numerical parameters of distance as well as of mass and charge so that the operator has geometric rather than full permutational symmetry. In the ultimate case, the only particle symmetry \mathcal{H} can show is the dynamical equivalence of particles of the same kind, the permutation symmetry. All interparticle coordinates must appear as operators; only mass and charge (and perhaps higher electric

⁷ E. B. Wilson, Jr., *J. Chem. Phys.* **3**, 276, 818 (1935).

⁸ N. F. Ramsey, *Nuclear Moments* (John Wiley & Sons, Inc. New York, 1953).

and magnetic moments) may appear as identifying parameters in an "exact" molecular Hamiltonian.

When restrictions of the small-oscillation variety are placed on the Hamiltonian, it no longer transforms as an invariant under the full rotation-permutation group \mathcal{G} , but rather, under some subgroup g . If g is a proper subgroup of \mathcal{G} , the irreducible representations γ of g are often no longer irreducible representations Γ of \mathcal{G} ; there are elements of \mathcal{G} excluded from g which can mix two or more γ 's to give a single Γ . Consequently, a matrix of \mathcal{H} which is diagonal in the approximation that g is the group, of \mathcal{H} is often not diagonal when all the group elements of \mathcal{G} are allowed. This is simply a way of saying that \mathcal{H} is only diagonal if the problem is solved, but perhaps it sheds light on the relation between restrictions on symmetry and the determination of stationary states.

The restrictions placed on operators appearing in \mathcal{H} reduce the complexity of a problem by letting the Hamiltonian carry some of the burden of describing the physical system which rightfully belongs to the wave function. The exact Hamiltonian should always transform under the totally symmetric representation of its full group \mathcal{G} . A wave function may transform under other irreducible representations of \mathcal{G} and therefore show how the physical system displays its geometric symmetry; the Hamiltonian cannot do this in general without violating the principle of the dynamical equivalence of particles of the same kind. (We can find simple special cases like molecules whose nuclei are all different, and homonuclear diatomics or equilateral-triangular triatomics whose Hamiltonians do satisfy the required permutation symmetry. No molecule containing four or more identical nuclei, however, can be entirely described by the small-oscillation model.⁹)

The foregoing argument has been introduced to show explicitly how a Hamiltonian matrix generally is nondiagonal if its basis functions were derived with restrictions on particle coordinates appearing in \mathcal{H} . Suppose we want to make an observation which utilizes or measures some dissimilarity in sites which identical nuclei may occupy. It is a well-known theorem that two Hermitean operators have simultaneous eigenfunctions if and only if they commute.⁹ This is easily restated to fit our present line of reasoning: if an Hermitean operator \mathcal{R} has eigenfunctions which are *not* basis functions for the irreducible representations of the Hamiltonian, then these functions are not eigenfunctions of \mathcal{H} . Therefore \mathcal{R} and \mathcal{H} do not commute. Hence any measurement of \mathcal{R} must be a measurement of a nonstationary state. This, together with the previous discussion, shows that *any state in which we can identify nonequivalent sites of identical nuclei must be a nonstationary state.*

⁹ E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), Sec. 37c, p. 28.

The degree to which a state is nonstationary is a matter of the energy separation of the actual stationary states, the permutation frequency, or the size of the potential barrier, or of the degree to which the Hamiltonian is nondiagonal in a representation based on eigenfunctions of \mathcal{R} . To see this, we write a matrix element of $[\mathcal{R}, \mathcal{H}]$ using basis functions ϕ_k such that

$$\mathcal{R}\phi_k = R_k\phi_k. \quad (1)$$

Then

$$(\phi_k | [\mathcal{R}, \mathcal{H}] | \phi_l) = (R_k - R_l) (\phi_k | \mathcal{H} | \phi_l), \quad (2)$$

vanishing when \mathcal{H} is diagonal.

We may measure any nonstationary property \mathcal{R} that we choose for a molecule, but if the stationary states are far from each other with respect to the ΔE associated with the time it takes to measure \mathcal{R} , then we observe essentially the expectation value $\langle \mathcal{R} \rangle$ characteristic of the stationary states. Even if the appropriate ΔE does cover a number of stationary states, these states may be based on a vast number of eigenstates of \mathcal{R} , or they may each be based on eigenstates of \mathcal{R} which contribute to none of the other stationary states. In either of these situations, we still learn little or nothing more than we would have by observing stationary states alone. If, however, the ΔE associated with a measurement of \mathcal{R} spans a set of stationary states which can combine to give a small number of eigenstates of \mathcal{R} , then direct observation of \mathcal{R} displays these eigenstates, whose properties often are quite different from those of the stationary states.

With the above discussion as a basis, we can look for molecules which might exhibit tunneling as a mechanism for establishing equivalences of identical nuclei. We simply look for molecules having identical nuclei occupying nonequivalent sites. The commonest of these are the hydrocarbons; in general, we expect tunneling rates for carbon nuclei in hydrocarbons to be extremely low, well below anything we could detect. Cations of hydrocarbons, however, have been observed to show rapid rearrangement in the gas phase. These rearrangements might be due to tunneling processes. The phosphorus pentahalides also might serve as examples. A number of these molecules have been studied with NMR techniques by Gutowsky et al.¹⁰ The tetragonal pyramids BrF_5 and IF_5 show two fluorine resonance peaks with intensities in the ratio of 4:1; these were assigned to the four fluorine nuclei of the base and the one at the apex, respectively, so that tunneling is not observed in these cases. The trigonal bipyramid PF_5 shows only one fluorine resonance peak (split into a doublet due to coupling to the phosphorus nucleus) despite the geometric nonequivalence of the equatorial and polar fluorines. Therefore the fluorine nuclei must all be occupying both kinds of sites, by

¹⁰ H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.* **21**, 279 (1953).

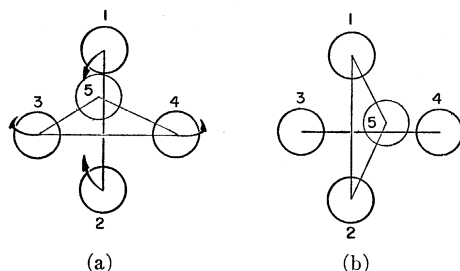


FIG. 2. Pseudorotation in a trigonal bipyramid. The apex atoms 1 and 2 of (a) move 15° out, while the equatorial atoms 3 and 4 move 15° back toward the plane of the paper.

means of either chemical exchange or a tunneling process. If tunneling does occur, a motion like that shown in Fig. 2 would accomplish the desired exchange; the motion as shown carries the molecule of Fig. 2(a) into a rotated, permuted form of itself.¹¹ This process might occur at a sufficiently high frequency so that all five fluorine nuclei are equivalent after a very short time interval, say 10^{-3} sec or less. If such a process does occur, it must be reconciled with the kinetic data for the PCl_5 molecule given by Downs and Johnson.^{12,13} They report that the chlorine atoms of PCl_5 , also a trigonal bipyramid, exhibit two different rates of exchange with isotopic chlorine; three Cl's exchange extremely rapidly, while the other two require ca 100 min for 90% reaction. A comparison of tunneling rates for PCl_5 and PF_5 , based on the WKB method as formulated by Dennison and Uhlenbeck,¹⁴ shows that the difference in mass, bond lengths, and vibration frequencies^{15,16} make the large difference in rates a reasonable one.¹⁷

Other molecules in which tunneling might be observed are ClF_3 , a bent-tee structure, and SF_4 , which has the C_{2v} structure of a highly distorted tetrahedron. These systems, which have been discussed by Muettterties and Phillips,^{18,19} have NMR spectra which are compatible with the tunneling hypothesis and even show transitions from single-line to multiple-line absorptions when the samples are cooled. These data are, however, at least as well explained in terms of chemical exchange (known to occur for ClF_3), and it is probably best to assume that tunneling has not yet been observed in these cases. The NMR data do require that the tunneling rates for both ClF_3 and SF_4 be con-

¹¹ This possibility was first brought to the attention of the author by Dr. Felix T. Smith.

¹² J. J. Downs and R. E. Johnson, *J. Chem. Phys.* **22**, 143 (1954).

¹³ J. J. Downs and R. E. Johnson, *J. Am. Chem. Soc.* **77**, 2098 (1955).

¹⁴ D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932). Also see references 2 and 3.

¹⁵ H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.* **20**, 1652 (1952).

¹⁶ J. K. Wilmhurst and H. J. Bernstein, *J. Chem. Phys.* **27**, 661 (1957).

¹⁷ R. S. Berry (to be published).

¹⁸ E. L. Muettterties and W. D. Phillips, *J. Am. Chem. Soc.* **79**, 322 (1957).

¹⁹ E. L. Muettterties and W. D. Phillips, *J. Am. Chem. Soc.* **81**, 1084 (1959).

siderably lower than for PF_5 . This is expected since, in the chlorine and sulfur compounds the heavy nuclei do not lie at the centers of mass and therefore must move when tunneling occurs. The tunneling frequency depends in such a sensitive way on the effective mass that the observed rates or limits on rates are quite compatible.

Still another example is cyclopentane. This molecule, whose carbon skeleton forms a puckered pentagon, has at any instant one unique carbon nucleus and two pairs of equivalent carbons. The motion which converts a unique carbon into a paired carbon corresponds to a permutation of the nuclei and a rotation of the pentagon. This process, often called pseudorotation, appears to have a measurable effect on the specific heat of cyclopentane.⁵

Our final example is perhaps the simplest case of a molecule, in which identical nuclei occupy nonequivalent sites. The isosceles triangle of ozone is amenable to more extensive study than the systems just mentioned and is the subject of the second part of this discussion.

TABLE I. Constants for the ozone molecule O_3 .¹⁶

Constant	Value
r_{0-0}^a	1.278 A
Apex angle ^a	$116^\circ 49'$
μ^a	0.53 debye
ν_1^b	1110 cm^{-1}
ν_2^b	705 cm^{-1}
ν_3^b	1043 cm^{-1}
f_d^c	5.7007 md/A
$f_{\alpha/d^{20}}$	1.2847 md/A
$f_{d\alpha/d^c}$	0.3324 md/A
f_{dd^c}	1.5233 md/A

^a See reference 24.

^b See reference 20.

^c See reference 23.

II. STATIONARY STATES AND TUNNELING IN THE OZONE MOLECULE

A. Description of the Problem

The structure of the ozone molecule is now well established on the grounds of infrared²⁰ and microwave²¹⁻²³ studies, and the vibrational constants have been determined.^{24,25} The molecule is an isosceles triangle with O-O bond lengths of 1.277 A and an angle of $116^\circ 49'$. The molecule has a dipole moment of 0.53 debye.²⁵ (Data pertinent to our discussion are collected for convenience in Table I.) This is clearly a case in which the apex position is quite different from the two base positions, so that the O_3 molecule does satisfy the condition of having nonequivalent sites for identical nuclei.

²⁰ M. K. Wilson and R. M. Badger, *J. Chem. Phys.* **16**, 741 (1948).

²¹ R. Trambarulo, S. N. Ghosh, C. A. Burrus, Jr., and W. Gordy, *J. Chem. Phys.* **21**, 851 (1953).

²² R. H. Hughes, *J. Chem. Phys.* **24**, 131 (1956).

²³ E. K. Gora, *J. Mol. Spectroscopy* **3**, 78 (1959).

²⁴ L. Pierce, *J. Chem. Phys.* **24**, 139 (1956).

²⁵ A. Danti and R. C. Lord, *J. Chem. Phys.* **30**, 1310 (1959).

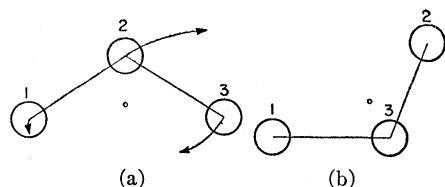


FIG. 3. Pseudorotation in an isosceles triangle. The pseudorotated figure (b) corresponds to sending (a) through a clockwise rotation of $\frac{2}{3}\pi$ and permuting nuclei 1→3, 3→2, and 2→1.

Some internal motion, such as that shown in Fig. 3, must be possible so that the equivalence of the oxygen nuclei can be established. Just as in the case of PF_5 or cyclopentane, the necessary motion is, in general, equivalent to a permutation of nuclei and a rotation of the molecule as a whole. We refer to such motion as pseudorotation, following the usage of reference 5. The success of the small-oscillation model and the large amplitudes of nuclear motion necessary to produce pseudorotation in ozone make it apparent that the process involves tunneling, and occurs at a frequency quite low relative to those for NH_3 or C_2H_6 , for example. In fact, we are faced with the question of whether tunneling in ozone could be observed at all.

In the two following sections, we investigate the tunneling problem. First we find a favorable path and estimate the potential barrier along this direction. Finally, we consider the possibility of observing tunneling in the ozone molecule.

B. Potential Barrier

We consider the molecule as shown in Fig. 3(a) and allow the nuclei to undergo large-amplitude motions. The molecule may reach a configuration which could have been attained equally as well from some other starting configuration, such as the permuted and rotated form shown in Fig. 3(b). When the nuclei return from their distorted configuration, they could return to the equilibrium configuration of Fig. 3(a) or to that of Fig. 3(b). The latter is the tunneling for which we seek. But there are infinitely many possible large-amplitude motions which could lead to tunneling; we must find the most favorable. That is, we must explore the full potential surface separating 3(a) from 3(b) and find the geometry and potential energy of that molecular configuration along the crest of the potential surface for which the potential energy is lowest; we want to find the saddle of the potential energy surface.

We assume that after tunneling has occurred the molecule is in a configuration derived by a cyclic (132) permutation of nuclei, followed by a rotation of $\frac{2}{3}\pi$. The permutation is a result of our choice of numbering and introduces no loss of generality. The $\frac{2}{3}\pi$ angle is chosen so that three applications of the clockwise pseudorotation carry a molecule back into itself. This is a real restriction, and there is no *a priori* reason

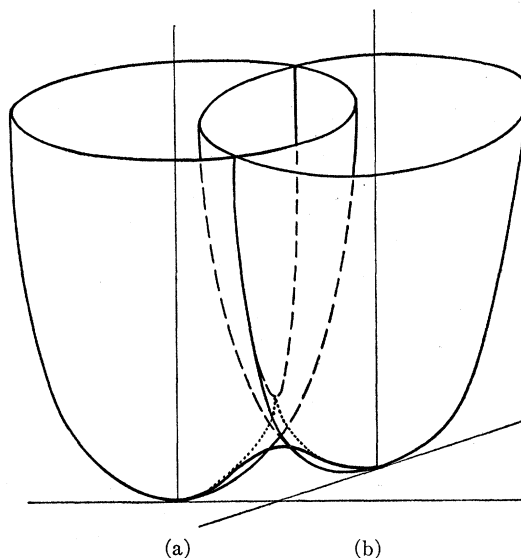


FIG. 4. The intersection of two paraboloids. The dotted line shows the path from one potential minimum to the saddle and down to the other minimum. The heavy smooth curve beneath it indicates the cosine curve used to approximate a realistic barrier.

why the most probable tunneling motion could not leave the molecule rotated by any angle ϕ . In fact, the angle ϕ could perfectly well be incommensurate with 2π so that no amount of pseudorotation in one direction would return the molecule to its original configuration. The restriction that $\phi = \frac{2}{3}\pi$ is introduced strictly for computational convenience.

In order to search the potential surface for a saddle, we assume that the molecular geometry at the true saddle point is essentially the same as it is beneath the saddle formed by the paraboloids of the normal harmonic vibrations. The normal coordinates of ozone have been determined by Pierce,²³ so that we can construct the harmonic potential hypersurfaces for the molecules of Fig. 3. These are shown schematically in Fig. 4; the figure can show surfaces for only two vibrations of each form and can therefore be no more than a crude analog of the real situation. The two surfaces intersect, and their surface of intersection is the crest of the barrier separating one form of the molecule from the other. Therefore, to find the saddle we do the following:

(a) express the normal coordinates Q'_k of the pseudorotated molecule as linear combinations of the normal coordinates Q_j of the original molecule;

(b) construct the expressions for the potential surfaces $V(Q')$ and $V(Q)$ and equate them to find their intersection;

(c) set equal to zero the derivatives of the equation of the intersection surface with respect to two of the normal coordinates Q_j ; and finally

(d) solve the simultaneous quadratic equations to determine the geometry of the saddle point.

Knowing the desired geometry, we may replace the

unrealistic parabolic potential with a much smoother one, suitably fitted, and estimate the barrier from the latter.

We have the potential of the original molecule:

$$2V(Q_1, Q_2, Q_3) = \lambda_1 Q_1^2 + \lambda_2 Q_2^2 + \lambda_3 Q_3^2, \quad (3a)$$

and similarly for the molecule after pseudorotation:

$$2V(Q_1', Q_2', Q_3') = \lambda_1 Q_1'^2 + \lambda_2 Q_2'^2 + \lambda_3 Q_3'^2. \quad (3b)$$

The normal coordinates Q_k' are most conveniently expressed as linear combinations of the original normal coordinates Q_j ,

$$Q_k' = \sum_1^3 a_k^j Q_j, \quad (4)$$

if we use a succession of transformations as indicated in the following. We simply express each coordinate set in terms of the set immediately following it, working our way from the final normal coordinates through symmetry coordinates and local Cartesian coordinates to center-of-mass Cartesian coordinates, and then back along the corresponding path to the initial normal coordinates. As symmetry coordinates we have used those of a valence force field, to correspond to the constants given by Pierce.²⁴

We have

Q' (normal coordinates)

↓

S' (valence force field symmetry coordinates)

↓

r' (local Cartesian coordinates, with origins at equilibrium positions of nuclei)

↓

R' (center-of-mass Cartesian coordinates)

↓

R (rotated center-of-mass Cartesian coordinates)

↓

r (local Cartesian coordinates)

↓

S (symmetry coordinates)

↓

Q (normal coordinates).

The actual transformations are completely straightforward⁴ and simply involve bookkeeping. For convenience we give two of the intermediate steps as well as the final transformation.

The normal coordinates Q_1 , Q_2 , and Q_3 can be expressed in terms of the symmetric stretching motion S_1

and bending motion S_2 and the asymmetric stretching mode S_3 :

$$Q_1 \times 10^{19} = 0.3602 S_1 + 0.2951 S_2, \quad (5a)$$

$$Q_2 \times 10^{19} = -0.0696 S_1 + 0.3273 S_2, \quad (5b)$$

$$Q_3 \times 10^{19} = 0.3287 S_3. \quad (5c)$$

The primed normal coordinates in terms of the unprimed local Cartesian coordinates are as follows: (The Cartesian coordinates are collected into symmetry coordinate form.)

$$Q_1' \times 10^{19} = 0.525 - 0.169(x_1 - x_2) - 0.293(y_1 - y_3) + 0.142(x_1 + x_2 - 2x_3) - 0.082(y_1 + y_2 - 2y_3), \quad (6a)$$

$$Q_2' \times 10^{19} = -0.461 - 0.046(x_1 - x_2) - 0.080(y_1 - y_2) + 0.306(x_1 + x_2 - 2x_3) - 0.177(y_1 + y_2 - 2y_3), \quad (6b)$$

$$Q_3' \times 10^{19} = 0.135 + 0.105(x_1 - x_2) - 0.061(y_1 - y_2) - 0.099(x_1 + x_2 - 2x_3) - 0.172(y_1 + y_2 - 2y_3). \quad (6c)$$

The entire transformation of primed normal coordinates into unprimed normal coordinates is as follows:

$$Q_1' = -0.525 - 0.077 Q_1 - 0.411 Q_2 + 0.943 Q_3, \quad (7a)$$

$$Q_2' = -0.461 - 1.199 Q_1 + 0.529 Q_2 + 0.975 Q_3, \quad (7b)$$

$$Q_3' = 0.135 + 0.065 Q_1 + 0.293 Q_2 - 0.194 Q_3. \quad (7c)$$

We substitute the preceding values into the equation

$$\lambda_1 Q_1^2 + \lambda_2 Q_2^2 + \lambda_3 Q_3^2 = \lambda_1 \left(\sum_0^3 a_1^i Q_i \right)^2 + \lambda_2 \left(\sum_0^3 a_2^i Q_i \right)^2 + \lambda_3 \left(\sum_0^3 a_3^i Q_i \right)^2. \quad (8)$$

This gives us a polynomial equation

$$f(Q_1, Q_2, Q_3) = 0. \quad (9)$$

We set

$$\left(\frac{\partial f}{\partial Q_1} \right)_{Q_2, Q_3} = 0 \quad \text{and} \quad \left(\frac{\partial f}{\partial Q_2} \right)_{Q_1, Q_3} = 0 \quad (10a, b)$$

and solve the three simultaneous equations. (Graphical solution was used.) These conditions give a saddle²⁶ at the points

$$Q_1 = -0.22 \times 10^{-19}, \quad (11a)$$

$$Q_2 = -0.380 \times 10^{-19}, \quad (11b)$$

$$Q_3 = 0.086 \times 10^{-19}. \quad (11c)$$

²⁶ The saddle point determined by the present method is not a point of symmetry; in fact,

$$\begin{aligned} Q_1' &= -0.27, \\ Q_2' &= -0.315, \\ Q_3' &= -0.007. \end{aligned}$$

This is at least in part due to the inaccuracy of the graphical solution of the equations but could also be due to flat regions of the surface of intersection. Note that the asymmetric Q_3' vibration has its sign opposite to that of Q_3 , corresponding to pseudorotation in the opposite direction.

These displacements have little intuitive significance in their present units, and are more easily understood if they are rescaled in units of their dimensionless classical vibration amplitudes Δ_1 , Δ_2 , and Δ_3 . These units prove useful later in evaluating tunneling frequencies also. In these terms, we have

$$Q_1 = -9.8\Delta_1, \quad (12a)$$

$$Q_2 = -13.5\Delta_2, \quad (12b)$$

$$Q_3 = 3.7\Delta_3. \quad (12c)$$

The paraboloid barrier at the saddle has a height $V_0 = 124\,000\text{ cm}^{-1}$. A more reliable estimate of the barrier height is probably that which we obtain when we replace the paraboloid surface with a cosine function

$$V = \frac{1}{2}V_0(1 - \cos\xi). \quad (13)$$

We determine the scale of ξ by requiring that $V_\xi = V = 0$ at $\xi = 0$, and that V_ξ reach its maximum at the saddle of V . We determine V_ξ^0 by first supposing that the path on the V surface from potential minimum directly to the saddle can be approximated as a simple parabola $V'(x)$ reaching $124\,000\text{ cm}^{-1}$ at the saddle, where $x = x_1$. We then require that V_ξ have the same second derivative as $V'(x)$ at the origin. That is,

$$V_\xi = \frac{1}{2}V_\xi^0[1 - \cos(\pi x/x_1)] \quad (14)$$

and

$$(\partial^2 V_\xi / \partial x^2)|_{x=0} = (\partial^2 V' / \partial x^2)|_{x=0}. \quad (15)$$

This gives

$$V_\xi^0 = (4/\pi^2)V_0, \quad (16)$$

so that the cosine barrier is 0.417 times as high as the parabolic barrier. In our case we find that V_ξ^0 is $51\,700\text{ cm}^{-1}$ or 148 kcal/mole . The parabolic and cosine curves are indicated in Fig. 4.

The value of 148 kcal/mole should be interpreted only as an order-of-magnitude estimate, not as a quantitative determination. The parabolic barrier value is probably reliable as an upper limit; it is unlikely that the true potential would rise more steeply than the paraboloid. The cosine curve has as its justification only its simplicity, its smooth form, and its success in representing potential barriers for hindered internal torsion.²⁷

C. Detection of Tunneling in Ozone

The ozone barrier of 150 kcal/mole is quite high by comparison with the 1- to 3-kcal barriers commonly observed for hindered rotors. In fact, it is quite improbable that tunneling occurs at any detectable rate in the ground state of ozone. This is shown by application of the WKB method as modified by Dennison and Uhlenbeck.¹⁴ They showed that if ν_0 is the vibrational frequency along the tunneling coordinate, m the

effective mass of the tunneling system, $V(m)$ its potential, and E its total energy, then the tunneling rate ν is given by

$$\nu = (\nu_0/\pi)e^{-I}, \quad (17)$$

with

$$I = \hbar^{-1} \int_{-s_0}^{s_0} \{2m[V(s) - E]\}^{1/2} ds. \quad (18)$$

The integration is carried out over the entire classically forbidden range of the displacement s which lies under the potential barrier. In the case of a cosine barrier, the integration may be carried out in terms of the complete exponential integrals $K(k)$ and $E(k)$. We find that

$$I = [4\sqrt{2}\pi^{-1}][x_1(mV_0\xi)^{1/2}\hbar^{-1}][E(k) - (E/V_0)K(k)], \quad (19)$$

with

$$k = [(V_0 - E)/V_0]^{1/2}. \quad (20)$$

In general, the form of the WKB approximation demands that the tunneling rate be of the form

$$\nu = \nu_0\pi^{-1} \exp[-\rho^2 f(\rho, E)], \quad (21)$$

where ρ is the distance from the equilibrium position to the potential maximum at the center of the barrier, measured in the dimensionless units of classical harmonic oscillator displacement amplitudes, and $f(\rho, E)$ is a very slowly varying function of ρ when $V_0 \gg E$. The tunneling rate for ozone in its ground state is then of the order of 10^{-90} sec^{-1} if we use the vector displacement determined in the last section, which gives $\rho \sim 17$. The rate depends sensitively on ρ and on the magnitude of $f(\rho, E)$; the latter, in turn, depends on the shape of the barrier. Since ν does depend so sensitively on ρ and f , we feel that no credence should be given to the value of the tunneling rate just given, except insofar as it gives an order-of-magnitude estimate of the exponent. The correct value of I could easily be smaller by a factor of 5 or even 10, but is very improbably a factor of 50 or 100 smaller than the estimated value.²⁸ The tunneling rate of course rises sharply as E increases, so that we should look for tunneling processes in excited vibrational states of ozone, if they are to be found at all. Polo²⁹ has pointed out that one might find indications of tunneling by observing excited-state transitions of the bending mode, whose fundamental frequency is 705 cm^{-1} .²⁰ The anharmonicity constant of this vibration might well be anomalous, so that as bending amplitudes get larger, it becomes easier to decrease the O-O-O angle. (The usual case corresponds to increasing mutual repulsions of the two outer atoms as the vibrational energy goes up.) Sufficiently highly excited states could perhaps be found in an electric discharge, possibly even in the discharge in which ozone is being produced.

²⁸ If, for example, we are successful in finding a much smaller ρ , perhaps taking the molecule into a form rotated by an angle other than $\frac{2}{3}\pi$, then this value might be very much diminished.

²⁹ S. R. Polo (private communication).

²⁷ D. R. Herschbach and J. D. Swalen, *J. Chem. Phys.* **29**, 761 (1958).

We turn to other methods of detecting tunneling in ozone, assuming now that the actual rate is low but not as low as our crude calculations indicated. Alternatively we may suppose that experiments may be performed with molecules in highly excited vibrational states. To carry out this examination we return to the problem of stationary states. Ozone is similar to the hindered rotors like ethane which have threefold symmetry. Any one oxygen nucleus may be at the apex of the triangle, so that there are three independent states with numbered nuclei assigned to specific sites. We label these ψ_1 , ψ_2 , and ψ_3 , with the subscript denoting which oxygen nucleus is in the unique position. As in the hindered rotor case, the stationary states are linear combinations of the ψ_j 's; we may write them as

$$\Psi_{\text{I}} = N_{\text{I}}(\psi_1 + \psi_2 + \psi_3), \quad (22a)$$

$$\Psi_{\text{II}} = N_{\text{II}}(\psi_1 + \exp(\frac{2}{3}\pi i)\psi_2 + \exp(-\frac{2}{3}\pi i)\psi_3), \quad (22b)$$

and

$$\Psi_{\text{III}} = N_{\text{III}}(\psi_1 + \exp(-\frac{2}{3}\pi i)\psi_2 + \exp(\frac{2}{3}\pi i)\psi_3). \quad (22c)$$

Only the first of these is totally symmetric with respect to all nuclear permutations; the latter two can be transformed into each other by exchanging nuclei 2 and 3, for example. The existence of the finite barrier causes Ψ_{I} to have an energy slightly different from Ψ_{II} and Ψ_{III} , and conceivably, a slow enough measurement would show this splitting. Most ordinary observations would, however, correspond much more closely to observations of the ψ_j 's than of the Ψ 's.

Let us consider an observation of ozone containing only O^{16} nuclei. In order that our results be detectably different from the observation of a true stationary state, the observed state would have to be a superposition of the stationary states. But the O^{16} nucleus is a Bose-Einstein particle of spin zero, so the stationary states of ozone must be totally symmetric with respect to nuclear permutations. Therefore, of the lowest three states, only Ψ_{I} can be populated, Ψ_{II} and Ψ_{III} can never contribute and there is no way of detecting a nonstationary state of O_3^{16} based on these three functions. Actually, this is almost a trivality; O^{16} has no electric or magnetic moments so it cannot be used as a probe; hence, there is no way of distinguishing the two kinds of sites with nuclear properties.

If pure O_3^{16} cannot betray its barrier in direct experiments, perhaps ozone containing O^{17} or O^{18} nuclei might. First, let us compare the molecule $\text{O}^{16}\text{-O}^{16}\text{-O}^{18}$ with pure $\text{O}^{16}\text{-O}^{16}\text{-O}^{16}$. The lower symmetry of the former permits it to occupy the rotational states forbidden to the latter, so that the unsymmetrical molecule has a richer microwave spectrum than the latter.

In the small-oscillation approximation, the molecule $\text{O}^{16}\text{-O}^{18}\text{-O}^{16}$ must satisfy the same selection rules as the pure O^{16} species. If tunneling is permitted, then the wave functions for $\text{O}^{16}\text{-O}^{18}\text{-O}^{16}$ and $\text{O}^{16}\text{-O}^{16}\text{-O}^{18}$ mix, and the strict selection rules of O_3^{16} no longer hold. Therefore we might expect "forbidden" lines of very low intensity to appear in the $\text{O}^{16}\text{-O}^{18}\text{-O}^{16}$ microwave spectrum, corresponding to transitions involving the "unallowed" levels. Again, it might be necessary to look at highly excited vibrational states in order to detect these weak lines.

One other technique suggests itself. The extremely high resolution of nuclear resonance might permit observation of tunneling. At first sight this seems straightforward; a sample containing $\text{O}^{16}\text{-O}^{16}\text{-O}^{17}$ and $\text{O}^{16}\text{-O}^{17}\text{-O}^{16}$ is examined. If one O^{17} resonance occurs, tunneling is relatively rapid; if two peaks appear, tunneling is slow. Like the molecules SF_4 and ClF_3 , however, ozone could suffer chemical exchange; or it could experience collision-induced tunneling. Both of these are likely processes in solution and would be difficult to distinguish from natural tunneling. Therefore a gas-phase study of the hyperfine spectrum of O_3 (containing O^{17}) would be less unambiguous.

Finally, McConnell³⁰ has pointed out that even the stationary states of ozone molecules containing one O^{17} should show two nuclear resonance frequencies, one appropriate to Ψ_{I} and the other, to Ψ_{II} and Ψ_{III} . This comes about because Ψ_{I} has symmetry differing from that of Ψ_{II} and Ψ_{III} and, in terms of perturbation theory, has a different set of nonvanishing matrix elements with higher excited states. Such a splitting would, in the case of ozone, be expected to be quite small compared with the splitting characteristics of the nonstationary states. Since ozone has a dipole moment of 0.53 debye unit,²⁵ the electrical environment of the unique apex oxygen is almost surely quite different from that of the two base oxygens. This suggests that the relative chemical shift of the two positions would be quite large in the nonstationary states. In all three stationary states, any one nucleus spends two-thirds of its time in a base position and one-third at the apex; the only way the stationary states can be affected in different ways is by means of second-order perturbation terms which distinguish their symmetries. Consequently, it seems reasonable (and we cannot say more than that) to expect a relatively large splitting of the O^{17} resonance, perhaps as much as 150 ppm for the nonstationary states, and a small splitting (indetectably small if we use PF_5 as an example¹⁵) for the stationary states.

³⁰ H. M. McConnell (private communication).