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Theoretical study of Fermi resonance in the vibrational spectrum of HO₂

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Fermi resonance complicates the vibrational spectrum of the hydroperoxyl radical, HO₂. Using a recent three-dimensional potential energy surface, we calculate vibrational wave functions for H-¹⁶O-¹⁶O and H-¹⁸O-¹⁸O. We identify low-lying Fermi resonant pairs and determine the degree of coupling by constructing linear combinations of these Fermi resonant wave functions. The coefficients are systematically varied to find the linear combination which, through visual inspection, replicates the nodal patterns of “pure” vibrational wave functions. The energies of the pure vibrational levels and the Fermi resonance shifts are also calculated. © 1995 American Institute of Physics.

INTRODUCTION

In a polyatomic molecule, there may be accidental degeneracy for vibrational levels of the same symmetry. The matrix elements which couple these vibrational states can range from large to vanishingly small. As a consequence of the coupling, observed vibrational levels are shifted from the unperturbed ones and the intensities of spectral bands are altered. Fermi¹ first elucidated accidental degeneracy between the (100) and (020) vibrational levels in the spectrum of CO₂. This phenomenon has since been observed by others for a variety of polyatomics.² Cases of accidental degeneracy need not involve the ν_1 and $2\nu_2$ levels but the term Fermi resonance is generally used.

Due to its importance as a mechanism for intramolecular energy transfer, Fermi resonance continues to be an active area of research.^{3–11} Recent work includes studies in the liquid phase,^{12–17} solid phase,¹⁸ and in physisorbed systems.^{19,20} Recent theoretical approaches to Fermi resonance include “algebraic resonance dynamics,”²¹ semiclassical,²² classical and quantum models^{23,24} of intramolecular vibrational energy redistribution.

In this paper, we discuss Fermi resonance for gas phase HO₂. There is accidental degeneracy between low-lying overtone and mixed-mode vibrational levels in the spectrum of H¹⁶O₂ and the fundamental and mixed mode vibrational levels in the spectrum of H¹⁸O₂. Very little is known about the vibrational spectrum of HO₂. The only reported vibrational levels are for H¹⁶O₂: ν_{001} =1097.6 (Ref. 25), ν_{010} =1391.7 (Ref. 26), ν_{100} =3426.2 (Ref. 27), and ν_{200} =6646.6 (Ref. 28) cm⁻¹. This is unfortunate because the hydroperoxyl radical is an important intermediate in atmospheric²⁹ and combustion³⁰ reactions. A recent comprehensive study³¹ has shown that HO₂ plays an even more important role in stratospheric ozone depletion than previously thought.

We calculated vibrational levels for HO₂ using a purely *ab initio* global potential energy surface which permits exchange of the H atom (proton transfer) between the two

equivalent O atoms.³² This surface was recently obtained by Dateo,³³ who fit the set of *ab initio* points calculated by Walch and Duchovic;³⁴ it is referred to here as the WDD surface.

For H-¹⁶O₂ levels calculated using the WDD surface, there is one instance of low-lying Fermi resonance: between the (200) and (015) levels, as noted previously.³² For isotopically substituted H-¹⁸O₂ levels, also calculated using the WDD surface, there is a stronger instance of low-lying Fermi resonance between the (100) and (012) levels. Both pairs of Fermi resonant levels are decoupled in the present investigation.

METHOD

Vibrational levels were calculated using the discrete variable representation-distributed Gaussian basis (DVR–DGB) technique,^{35,36} which, for the states studied, gives levels converged to within 0.1 cm⁻¹. We used the recent high-level WDD *ab initio* surface,^{33,34} and Jacobi coordinates (r, R, γ) as in Ref. 32. In these coordinates, \mathbf{r} is the O–O vector, \mathbf{R} is the center of mass of O–O to H vector, and γ is the angle between \mathbf{r} and \mathbf{R} . For this molecule, Jacobi or atom–diatom coordinates are an appropriate choice since the H-atom motion is largely decoupled from that of the heavier oxygen atoms. Wave functions associated with some of the HO₂ levels are shown in Figs. 4–6 of Ref. 32. Nodal patterns of the fundamental wave functions have distinctive features; their appearance in R/r (fixed γ) space is discussed in detail in Ref. 32.

During the course of that investigation, it was observed that occasionally two vibrational levels deviated from an expectedly regular progression, which would have resulted in near degeneracy of these levels. Instead, because the two levels were wave functions of the same symmetry, they coupled in Fermi resonance to form the vibrational wave functions Ψ_{FR1} and Ψ_{FR2} .

Our object is to decouple the Fermi resonant levels by constructing the “pure” (uncoupled) wave functions from which the Fermi resonant levels can be considered to arise.

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Because we use a morphing technique to obtain them, we refer to the decoupled wave functions as Ψ_{M1} and Ψ_{M2} . Specifically, we take linear combinations:

$$\Psi_{M1} = c_1 \Psi_{FR1} - c_2 \Psi_{FR2}, \quad (1)$$

and

$$\Psi_{M2} = c_2 \Psi_{FR1} + c_1 \Psi_{FR2},$$

where $c_1^2 + c_2^2 = 1$.

We use software that is designed to efficiently represent and perform simple algebra for large three-coordinate datasets on a uniform grid.³⁷ This visualization aid permitted us to compare simultaneously, and in detail, the nodal patterns and probability densities of the fundamental wave functions, as determined in Ref. 32, with Ψ_{FR1} , Ψ_{FR2} , and linear combinations thereof. Trial coefficients c_1 and c_2 were changed systematically until, through visual inspection, the trial Ψ_{M1} and Ψ_{M2} replicated the nodal patterns of “pure” vibrational wave functions. The finite ability to distinguish between a range of trial wave functions leads to uncertainty in these coefficients. We comment further on sources of error in visual inspection techniques below.

In the case of H-¹⁶O₂, the uncoupled wave functions were known *a priori* to be Ψ_{200} and Ψ_{015} but prior to morphing, neither wave function in the Fermi resonant pair was clearly assignable.

RESULTS

Figure 1 shows six panels of wave functions plotted on a grid of r vs R , with γ fixed at the equilibrium value of 47°. The pure O–H stretch fundamental, Ψ_{100} , shown in panel (a), has a single nodal plane which traverses the wave function at $R=2.52$ bohr. The energy, E_{100} , of this level is 3517 cm⁻¹ above the zero-point energy. The second OH overtone, Ψ_{300} , shown in (b), has three nodal planes at $R=2.32$, 2.60, and 2.92 bohr. The energy, E_{300} , of this level is 9794 cm⁻¹.

The energy, E_{200} , of the first O–H overtone is predicted by interpolation to lie at an intermediate value of ~ 6790 cm⁻¹. The Ψ_{200} nodal pattern is expected to be as simple as those of panels (a) and (b) with two nodal planes. However, the energy of the mixed mode (015) level is also predicted to lie close to this value. Three-dimensional exact calculation of the low-lying levels for H¹⁶O₂ showed a pair in Fermi resonance at $E_{FR1}=6786$ and $E_{FR2}=6793$ cm⁻¹. The corresponding wave functions, Ψ_{FR1} and Ψ_{FR2} , are shown in panels (c) and (d). It may be seen that their nodal patterns are too complicated for straightforward assignment, which is characteristic of Fermi resonance. These wave functions were morphed until their linear combination, Ψ_{M1} , gave the “pure” wave function, Ψ_{200} , which is shown in panel (e). Its nodal planes occur at 2.42 and 2.74 bohr. Its orthogonal complement, Ψ_{M2} , is shown in panel (f). The nodal pattern is recognizable as that of the “pure” wave function Ψ_{015} .

The coefficients (± 0.02) for the Fermi resonant pair were found to be:

$$\begin{aligned} \text{“}\Psi_{200}\text{”} &= 0.83\Psi_{FR1} - 0.55\Psi_{FR2}, \\ \text{“}\Psi_{015}\text{”} &= 0.55\Psi_{FR1} + 0.83\Psi_{FR2}. \end{aligned} \quad (2)$$

We designate the pure morphed wave functions in quotations to emphasize that they are not eigenfunctions of the full 3D Hamiltonian and have been determined by the above decoupling technique.

The degree of perturbation inherent in the Fermi resonance, which uses a zeroth-order coupling, can be calculated approximately using techniques such as in Ref. 38. The degree of perturbation is calculated numerically in the present approach by substituting the linear combinations of Eq. (2) into the eigenvalue equation in order to determine E_{M1} and E_{M2} . Thus $E_{M1}=6788.2$ and $E_{M2}=6790.8$ cm⁻¹, and the Fermi resonance shift is $E_{M1}-E_{FR1} (=E_{FR2}-E_{M2})=2.2\pm 0.2$ cm⁻¹. The Fermi coupling matrix element $\langle\Psi_{M1}|\mathcal{H}|\Psi_{M2}\rangle$ is found to be 3.2 ± 0.2 cm⁻¹. The degree of mixing is significant and suggests that the (015) \rightarrow (000) transition might be observed in the overtone spectrum of H¹⁶O₂.²⁸

The morphing technique described above is easily extended to Fermi resonance in other triatomics but the extension to Fermi resonance in polyatomics such as CH bend stretching in CHX₃ systems may prove problematic.

ISOTOPIC SUBSTITUTION

The approach presented above can be applied with equal success to H-¹⁸O₂. Three-dimensional exact calculation of the low-lying levels showed a pair in Fermi resonance at 3497 and 3517 cm⁻¹. The identities of these levels are known to be (012) and (100) but we emphasize that the morphing technique works even without knowledge of the resonant levels, as long as nodal patterns can be observed.

Figure 2 shows, in panels (a) and (b), contour plots of Ψ_{FR1} and Ψ_{FR2} . These wave functions appear to be inextricably mixed, but panels (c) and (d) show that a clear assignment has been made using the morphing technique. The coefficients (± 0.05) for the Fermi resonant pair were found to be

$$\begin{aligned} \text{“}\Psi_{012}\text{”} &= 0.70\Psi_{FR1} - 0.71\Psi_{FR2}, \\ \text{“}\Psi_{100}\text{”} &= 0.71\Psi_{FR1} + 0.70\Psi_{FR2}. \end{aligned} \quad (3)$$

Note that these coefficients indicate a level of mixing greater than that of the previous case. This is reflected in the larger Fermi resonance shift of $E_{M1}-E_{FR1} (=E_{FR2}-E_{M2})=9.8\pm 1.4$ cm⁻¹ and in the larger Fermi coupling matrix element, 10.0 ± 1.4 cm⁻¹.

SOURCES OF ERROR

Unlike previous methods used to estimate the Fermi resonance shift via an approximate 1D Hamiltonian, we emphasize that the present method, which uses the full 3D Hamiltonian, is exact. Accuracy in the present calculation is limited only by the accuracy of the morphing coefficients and the 3D potential energy surface. The errors inherent in the latter are discussed in greater detail in Refs. 32–34.

The most serious criticism of visual methods is that the human element involved in distinguishing trial wave functions depends on the experience and prejudice of the viewer. As such, the morphing procedure described here is not completely reproducible nor entirely quantifiable. For example, the coefficients in the strong-mixing case have an uncertainty

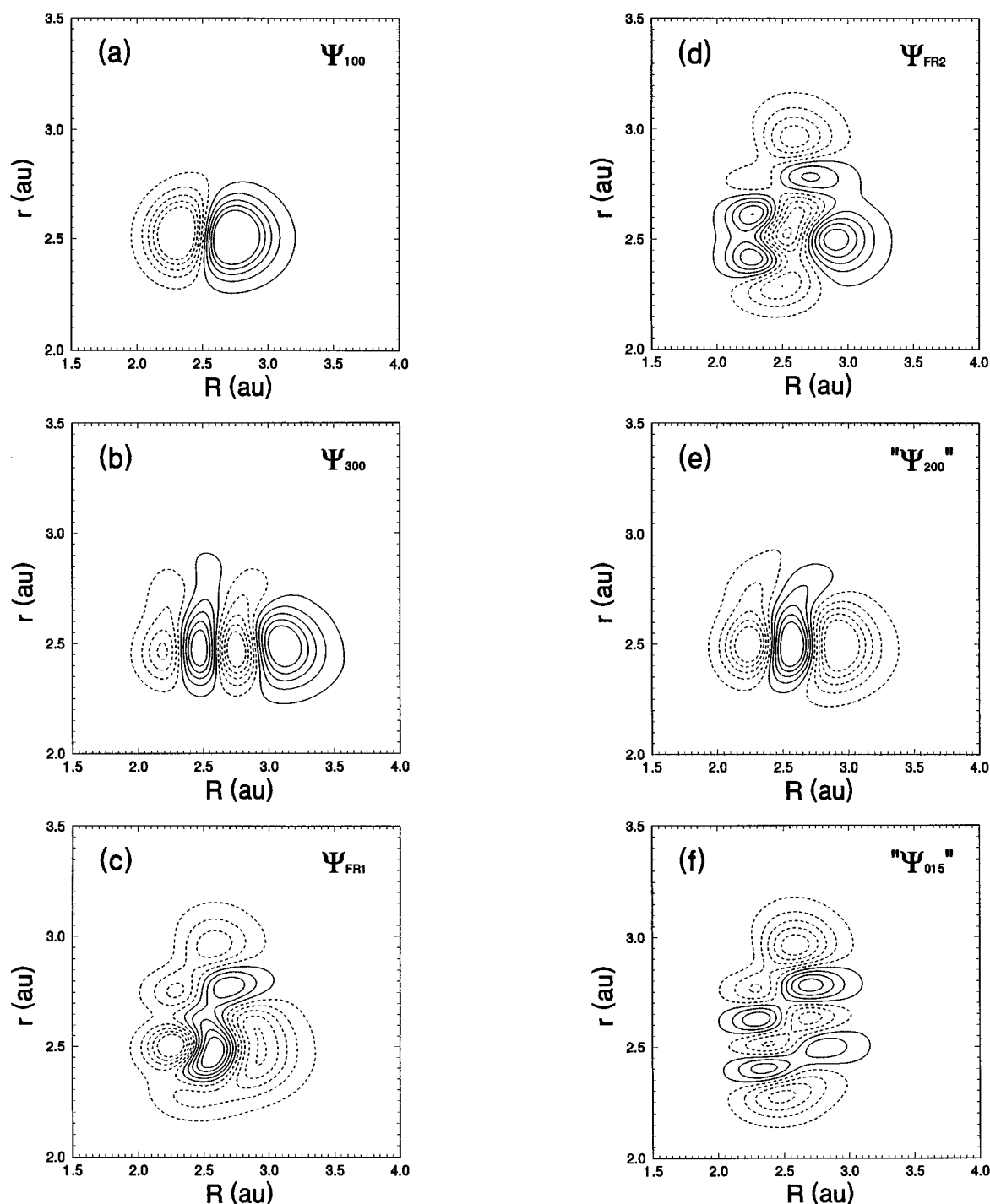


FIG. 1. Contour plots in the (r, R) plane of selected wave functions for H¹⁶O₂ at the equilibrium value of γ (47°). Contour intervals from -9 to 9 a.u., in 2 a.u. increments, are shown, with negative contours broken. (a) ν_1 at 3517 cm^{-1} above the zero-point energy; (b) $3\nu_1$ at 9794 cm^{-1} ; (c) Fermi resonant wave function at 6786 cm^{-1} ; (d) Fermi resonant wave function at 6793 cm^{-1} ; (e) combination wave function created from (c) and (d) which is attributed to $2\nu_1$; (f) orthogonal complement which is attributed to $\nu_2 + 5\nu_3$. Coefficients as noted in text.

greater than those in the moderate-mixing case. This uncertainty reflects the gap in deciding which of two approximately vertical planes which traverse Figs. 2(c) and (d) is more important. When $c_1 > 0.7$, the nodal plane in (c) is less prominent; when $c_1 < 0.7$, the nodal plane in (d) is less prominent. The value selected, $c_1 = 0.7$, reflected our judgment that the appearance of both planes be given equal

weight, even though panel (c) has two additional nodal planes to constrain the selection.

Quantification of such complex observations may be possible if we consider the problem in terms of a visual interpretation algorithm, such as those embodied in neural networks (NN). Such an approach would involve “training” of the NN on assigned wave function representations.

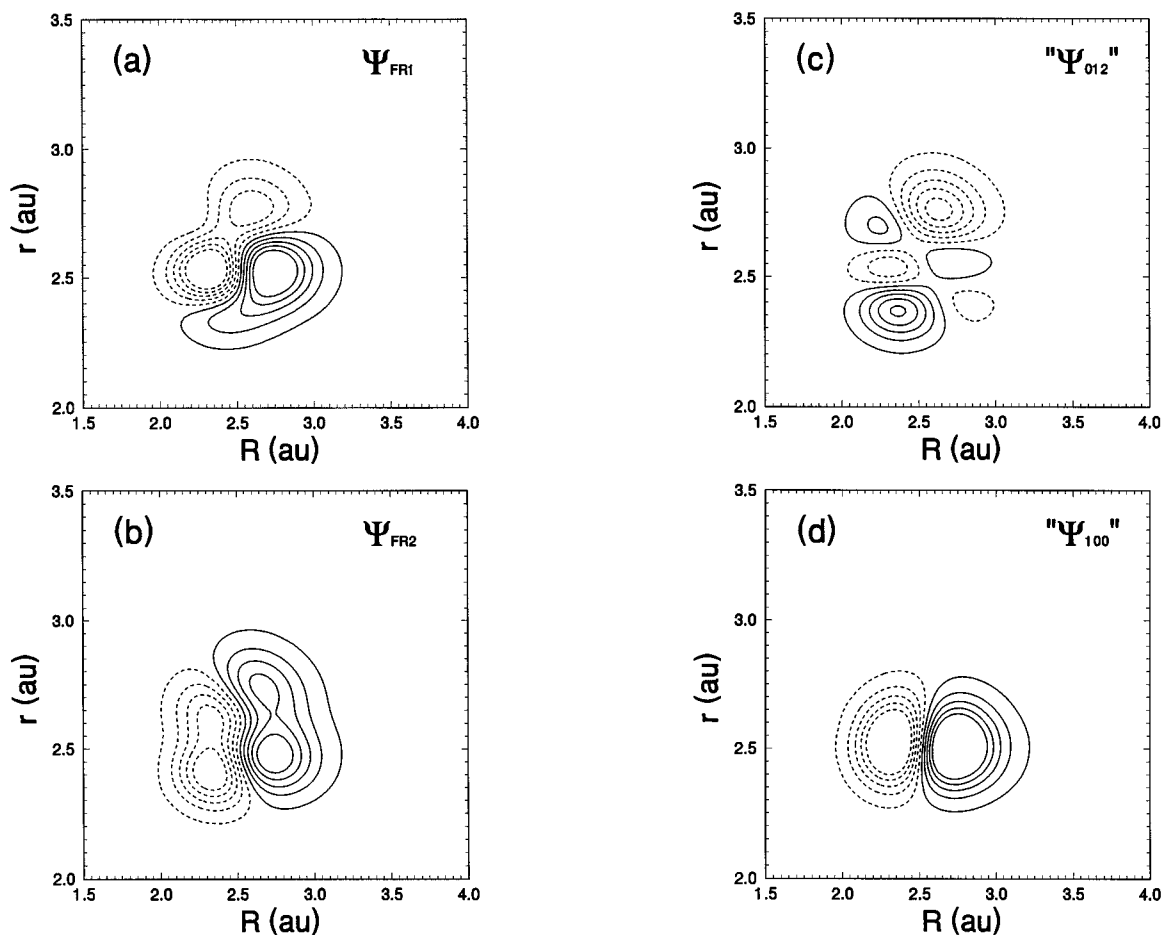


FIG. 2. Contour plots in the (r, R) plane of selected wave functions for H¹⁸O₂; γ angle and contour intervals as in Fig. 1. (a) Fermi resonant wave function at 3497 cm⁻¹; (b) Fermi resonant wave function at 3517 cm⁻¹; (c) combination wave function created from (a) and (b) which is attributed to $\nu_2 + 2\nu_3$; (d) orthogonal complement which is attributed to ν_1 . Coefficients as noted in text.

CONCLUSIONS

We report two examples of low-lying Fermi resonant pairs for the HO₂ molecule, based on a 3D calculation using a recent high-quality surface. We have presented a visual method, the morphing technique, for determining the degree of mixing of the Fermi resonant levels. This allows us to obtain the “pure” decoupled wave function which would have been present in the absence of Fermi resonance. Using this morphing technique, we have calculated the Fermi resonance shifts for low-lying vibrational levels of both H¹⁶O₂ and H¹⁸O₂.

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