The Self-Consistent-Field Approach to Polyatomic Vibrations

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Interest in the vibrational motion of molecules is pervasive in chemistry. Our view of this motion is based on the Born–Oppenheimer approximation which separates the motion of the electrons from that of the nuclei. The electronic motion produces an effective potential which holds molecules together and governs their vibrational motion. The complexity of this potential gives rise to the richness of much of chemistry. Thus, a theoretical picture of the vibrations of molecules is at the heart of many chemical questions.

The traditional view of vibrational motion is based on an harmonic approximation to the full nuclear potential. This very simple approximation gives rise to an extraordinarily simple and useful picture of vibrational motion, namely, that of independent vibrational modes, termed normal modes.[1] The vibration of each of these modes is governed by a simple one-dimensional harmonic potential. The utility and popularity of the normal-mode-harmonic-oscillator (NMHO) model derives from its power and the ease with which a normal mode analysis can be carried out. Because the theory is based on an harmonic potential the wave functions, energies, etc. are all known analytically. Thus the theory gives analytical expressions for many important quantities, such as infrared transition frequencies and selection rules,[2] partition functions,[3] and through them many important thermodynamic properties. In addition to its pervasive use in IR spectroscopy, the NMHO model has been used extensively in the theory of vibrations of solids[4] and solid surfaces,[5] polymers,[6] and proteins.[7] The model also plays a key role in the transition-state theory of activated rate processes.[8]

As with all approximate theories, the NMHO model has its limitations, some of which are quite serious. For example, consider breaking a bond. This simple but important process cannot be described by this model. First, an harmonic potential cannot lead to dissociation. Second, and more serious, bond breaking cannot be described by the motion of a single normal mode. If one examines the normal modes of vibration of a molecule with three or more atoms, one sees that none will describe the motion of a single bond. Rather, they describe the collective (and frequently beautiful) motion of all of the atoms in the molecule. Thus, exciting a single normal mode cannot result in a simple bond breaking without the participation, via coupling, of other normal modes.

Joel M. Bowman was born in Boston in 1948 and raised in Brookline, MA. He received an A.B. degree from the University of California at Berkeley in 1969 where he was admitted to Phi Beta Kappa. In 1974, he received his Ph.D. degree in Chemistry from Caltech under the guidance of Professor Aron Kuppermann. That year he joined the Chemistry Department of Illinois Institute of Technology and remained there until 1986. During most of that time he was also a faculty appointee at Argonne National Laboratory. He received an Alfred P. Sloan Fellowship in 1977. As of September 1986, he will be Professor of Chemistry at Emory University. His major research interests are the theory of molecular collision dynamics and lately the vibrational and rotational motion of molecules in the gas phase and on solid surfaces. He dedicates this article to his wife Barbara.

The eventual breakdown of the NMHO model is expected on general theoretical grounds simply because the harmonic approximation to the potential will eventually break down. When that happens, two very striking changes occur in the vibrational motion. First, the harmonic model for the normal modes deteriorates. Second, and more significant, there is a coupling among the normal modes. This coupling is very important for processes in chemistry which are only recently being studied by high-power lasers, for example. One now has the ability to pump large amounts of energy into a molecule and then probe a chemical change. One very beautiful example of this type of experiment is work by the Crim group in which high overtones of OH are excited in H_2O_2 followed by O–O bond rupture giving two OH radicals.[9] Thus, much of the energy initially deposited in the OH bond finds its way into the weaker O–O bond. Clearly, this process requires substantial coupling among the normal modes of vibration of H_2O_2. Indeed the general area of mode-specific chemistry, of which the above experiment is just one example, is currently faced with a prima facie breakdown of the NMHO model. There is currently a very intensive theoretical effort to explore the consequences of the breakdown of the NMHO model and to find something to replace it with. Our efforts have focused on a method which satisfies the following criteria. It should be general, accurate, and readily applicable to large systems. Traditional methods to go beyond the NMHO model are based on second order perturbation theory and standard configuration interaction methods.[10] Neither of these methods satisfy all of the above criteria.

In this Account we review a new theory[10–14] which deals with the full potential instead of approximating

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it by an harmonic potential. However, the vibrational wave function is approximated in a way that, in form, is exactly like the one used in the NMHO model. The theory is termed the *vibrational self-consistent-field theory* (VSCF) because, as we shall show, it is completely analogous to the self-consistent-field theory used extensively in electronic structure calculations. In the next section we review this theory and then present several examples and conclude with some remarks about its future uses.

The Vibrational Self-Consistent-Field Theory

The basic idea underlying the VSCF approach is very simple. For concreteness consider a three-mode system (e.g., a nonlinear triatomic molecule) and let the vibrational wave function for a quantum state $|l,m,n\rangle$ be represented as a simple product function

$$\Psi_{l,m,n}(Q_1,Q_2,Q_3) = \phi_l(Q_1)\phi_m(Q_2)\phi_n(Q_3) \quad (1)$$

where Q_1, Q_2, and Q_3 are the three normal coordinates. This *form* for the vibrational wave function is the same as the one in the NMHO model. Also, note that normal coordinates are a well-defined set of coordinates even when the NMHO model breaks down. Now, we seek the variationally best form of the *modal* wave functions $\phi_l(Q_1)$, $\phi_m(Q_2)$, and $\phi_n(Q_3)$. This is achieved by requiring that the expectation value of the full hamiltonian H, $\langle\Psi_{l,m,n}(Q_1,Q_2,Q_3)|H|\Psi_{l,m,n}(Q_1,Q_2,Q_3)\rangle$ be stationary with respect to small variation in each of the modals subject to the constraint that each modal be normalized. This approach is exactly analogous to the Hartree theory of electronic structure.[15] In electronic structure theory it is necessary to antisymmetrize the wave function and the resulting theory is termed Hartree–Fock theory. In the vibrational problem antisymmetrization is not necessary because the vibrational modes are distinguishable.

To proceed we express H as

$$H = h_1 + h_2 + h_3 + V_c(Q_1,Q_2,Q_3) \quad (2)$$

where h_i is a single-mode hamiltonian. For example,

$$h_i = T_i + V_i(Q_i),\ i = 1\text{–}3 \quad (3)$$

where T_i is the kinetic energy operator of the ith mode and $V_i(Q_i)$ is the single mode part of the full potential $V(Q_1,Q_2,Q_3)$. Thus,

$$V(Q_1,Q_2,Q_3) = V_1(Q_1)+V_2(Q_2)+V_3(Q_3)+V_c(Q_1,Q_2,Q_3) \quad (4)$$

and therefore V_c is the part of V which explicitly involves coupling among the modes. From the variational procedure mentioned above, the equations which the modals satisfy are

$$[h_1 + \langle\phi_m\phi_n|V_c(Q_1,Q_2,Q_3)|\phi_m\phi_n\rangle - \epsilon_l]\phi_l(Q_1) = 0 \quad (5a)$$

$$[h_2 + \langle\phi_l\phi_n|V_c(Q_1,Q_2,Q_3)|\phi_l\phi_n\rangle - \epsilon_m]\phi_m(Q_2) = 0 \quad (5b)$$

$$[h_3 + \langle\phi_l\phi_m|V_c(Q_1,Q_2,Q_3)|\phi_l\phi_m\rangle - \epsilon_n]\phi_n(Q_3) = 0 \quad (5c)$$

The matrix element $\langle\phi_m\phi_n|V_c(Q_1,Q_2,Q_3)|\phi_m\phi_n\rangle$ means that the integration is done over the two coordinates Q_2 and Q_3 and the quantity which results after integration is only a function of Q_1. Thus, it is useful to define effective potentials as follows:

$$V_{mn}(Q_1) = V_1(Q_1) + \langle\phi_m\phi_n|V_c(Q_1,Q_2,Q_3)|\phi_m\phi_n\rangle \quad (6a)$$

$$V_{ln}(Q_2) = V_2(Q_2) + \langle\phi_l\phi_n|V_c(Q_1,Q_2,Q_3)|\phi_l\phi_n\rangle \quad (6b)$$

$$V_{lm}(Q_3) = V_3(Q_3) + \langle\phi_l\phi_m|V_c(Q_1,Q_2,Q_3)|\phi_l\phi_m\rangle \quad (6c)$$

These potentials depend explicitly on only one modal coordinate Q_i, and they consist of the "diagonal part" of the potential $V(Q_1,Q_2,Q_3)$ plus the coupling potential averaged over the modal wave functions of the remaining modes. In terms of these effective potentials, eq 5 can be rewritten as

$$[T_1 + V_{mn}(Q_1) - \epsilon_l]\phi_l(Q_1) = 0 \quad (7a)$$

$$[T_2 + V_{ln}(Q_2) - \epsilon_m]\phi_m(Q_2) = 0 \quad (7b)$$

$$[T_3 + V_{lm}(Q_3) - \epsilon_n]\phi_n(Q_3) = 0 \quad (7c)$$

These appear to be simple one-dimensional eigenvalue equations with energy eigenvalues ϵ_l, ϵ_m, and ϵ_n. However, they are coupled because the effective potential for any one of them depends on the modal eigenfunctions of the other eigenvalue equations. A very convenient way to solve them is by an iterative procedure until self-consistency is achieved. In practice a zero-order set of modal wave functions, $\phi_l^0(Q_1)$, $\phi_m^0(Q_2)$, and $\phi_n^0(Q_3)$, are used to evaluate the effective potentials in eq 7. The eigenvalue equations are then solved, from which new modal eigenfunctions and eigenvalues are obtained. These modal eigenfunctions are then used to calculate new effective potentials which are then used to obtain new modal eigenfunctions and eigenvalues. The process continues until convergence is achieved, that is, when the modal wave functions used to obtain the effective potentials are the same as the ones calculated by solving the eigenvalue equations using those potentials. Thus, convergence is achieved when the iteration process becomes self-consistent and hence the name "self-consistent field" derives from the method used to solve the coupled equations, 7. In practice, the convergence criterion is that the eigenvalues ϵ_l, ϵ_m and ϵ_n do not change upon further iteration. Typically ten or so iterations are needed to achieve relative convergence of the eigenvalues to 10^{-6}.

In general, the zero-order modal wave functions are eigenfunctions of the hamiltonians h_i or the normal-mode-harmonic-oscillator wave functions. In the present context these are just the eigenfunctions of h_i with an harmonic approximation to the potentials $V_i(Q_i)$. We have solved[11–14] the eigenvalue equations numerically by using standard techniques such as the Finite-Difference-Boundary-Value method[16] and the Cooley–Numerov method.[17] Another approach which we currently use[18] is to expand the modals in a convenient basis, e.g., for the first mode

$$\phi_l^0(Q_1) = \sum\chi_j(Q_1)c_{jl} \quad (8)$$

where the $\chi_j(Q_1)$ are the normal mode eigenfunctions. Another choice we have frequently made is to use the anharmonic basis defined as the eigenfunctions of h_i. This basis is not analytically known in general and so each member of that basis is itself typically expanded in terms of an harmonic basis.

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In any case, expanding $\phi_l(Q_1)$, $\phi_m(Q_2)$ and $\phi_n(Q_3)$ in bases results in a set of coupled algebraic equations for the expansion coefficients in exact analogy with the Roothan implementation of the Hartree–Fock theory of electronic structure.[19] The basis set approach is favored especially when the coupling potential is represented as a multidimensional polynomial, in which case the matrix elements in eq 6 can be done analytically.

Finally, the energy of the VSCF state $\phi_l(Q_1) \times \phi_m(Q_2)\phi_n(Q_3)$ is

$$E_{l,m,n} = \langle \phi_l(Q_1)\phi_m(Q_2)\phi_n(Q_3)|H|\phi_l(Q_1)\phi_m(Q_2)\phi_n(Q_3)\rangle \quad (9)$$

$$= \epsilon_l + \epsilon_m + \epsilon_n - 2\langle \phi_l(Q_1)\phi_m(Q_2)\phi_n(Q_3)|V_c|\phi_l(Q_1)\phi_m(Q_2)\phi_n(Q_3)\rangle \quad (10)$$

We have written and submitted to the Quantum Chemistry Program Exchange a general code, called "POLYMODE", which calculates VSCF energies and wave functions for molecules as large as pentaatomics.[20] This code is available to the general community.

Beyond the VSCF Theory

The eigenvalue equations, eq 7, define the variationally best modals $\phi_l(Q_1)$, $\phi_m(Q_2)$, and $\phi_n(Q_3)$ for the quantum state $|l,m,n\rangle$. In addition to these modal wave functions they yield a complete set of "virtual" modals for each mode, that is, other modal wave functions which are labeled by quantum numbers which differ from l, m, and n. These virtual modals can be used as an expansion basis to perform a "configuration-interaction (CI)" calculation which, if converged, yields the exact vibrational eigenvalues and eigenfunctions of the full hamiltonian. We term this approach the VSCF-CI method.[12-14,21] Alternatively, one could do perturbation theory assuming that the VSCF wave function is the zero-order function. Both of these approaches are analogous to methods developed in electronic structure theory. Also, in analogy with a method from that field,[22] a multiconfiguration (vibrational) self-consistent-field theory has been suggested.[13] Such a theory may be useful if there are two (or more) VSCF configurations with nearly equal energies. Thus, the VSCF theory can be used as a launching point for techniques which are, in principle, exact.

A Word about Semiclassical VSCF Theory

A very interesting modification of the VSCF method just described is its semiclassical limit, as developed initially by Ratner, Gerber, and co-workers.[23] They noted that because the quantum VSCF eigenvalue equations are one-dimensional, their semiclassical solution would simply be the well-known semiclassical quantization method for one-dimensional systems. The extension they had to make was to derive a semiclassical expression for the effective potentials. This was done by using "primitive" semiclassical wave functions. Then the eigenvalue equations, 7, are solved during each iteration by applying the semiclassical quantization condition

$$\int P_i dQ_i = (n_i + 1/2)h \quad (11)$$

to each mode, where P_i is the classical momentum and the integral is over a complete classical orbit. The energy of the ith mode is then adjusted so that the n_i are the desired integers corresponding to the quantum state. There are applications where the primitive semiclassical wave functions are inadequate, as Farrelly et al.[24] and Farrelly[25] have recently pointed out. Farrelly has extended the semiclassical VSCF method to use more accurate semiclassical wave functions in these cases.

Before going on to discuss several examples where the VSCF theory has been applied, we should make some general comments on its generality and limitations. First, to its generality—the method does not depend on the choice of coordinates used to describe the vibrational motion. The use of normal coordinates in the above example was chosen for convenience in describing the method. Indeed it was clear from the outset that an optimum choice of coordinates would be one in which the VSCF method produces the lowest energy for a given state. (This second type of optimization has been explored in a limited way.[26-28]) Also, we have said very little about the nature of the coupling potential V_c. In fact, it too can be completely general, although most applications have used very simple multinomial expressions. Finally, the theory is capable of dealing with a large number of coupled modes in a computationally feasible manner. This is because the number of coupled eigenvalue equations to solve grows linearly with the number of modes in contrast to CI methods which grow exponentially with the number of modes.

Now to its limitations. Obviously, the exact vibrational wave function cannot be written as a simple product function. This is especially evident when there are two VSCF states (of the same symmetry) which are nearly energetically degenerate. These states can be expected to mix strongly. Nevertheless, it may turn out that simply allowing just those states to mix will produce a very accurate result. (We shall see an example of this later.) Another example where mixing is inherently important is for vibrational states which are metastable, that is, states which have energy above the energy needed to fragment the molecule, i.e., to break bonds. Even in "zero-order" two wave functions are needed to describe this situation, one to characterize the quasibound state and another to describe the continuum state. As noted above, mixing of VSCF states has been done in several studies (some are described in the next section), and so it is quite feasible to describe those processes which mandate mixing.

Application to the Water Molecule

In the first application we wish to answer the question, how well does the VSCF method work? To answer

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(21) Thompson, T. C.; Truhlar, D. G. *Chem. Phys. Lett.* **1980**, *75*, 87.
(22) See, for example: Wahl, A. C.; Das, G. In Modern Theoretical Chemistry; Schaefer, H. F., III, Ed.; Plenum: New York, 1977, Vol. 3.
(23) For a review, see: Ratner, M. A.; Gerber, R. B. *J. Phys. Chem.* **1986**, *90*, 20.
(24) Farrelly, D.; Hedges, R. M.; Reinhardt, W. P. *Chem. Phys. Lett.* **1983**, *96*, 599.
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(27) Thompson, T. C.; Truhlar, D. G. *J. Chem. Phys.* **1982**, *77*, 3031.
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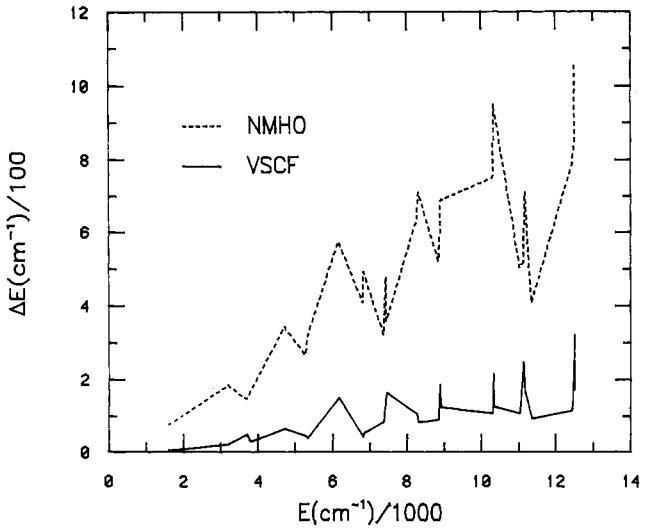

Figure 1. The error in normal-mode-harmonic-oscillator (NMHO) and vibrational self-consistent-field (VSCF) energies, ΔE, vs. the energy for three-mode H_2O.

this question we will consider a realistic model for nonrotating three-mode water. We used a fit to high-quality ab initio quantum mechanical calculations by Bartlett et al. of the electronic energy.[29] This fit is an 18-term fourth-order multinomial expansion in terms of the three normal coordinates, Q_1 (the symmetric stretch), Q_2 (the asymmetric stretch), and Q_3 (the bend),

$$V(Q_1,Q_2,Q_3) = \sum_{j+k+l\leq 4} C_{j,k,l} Q_1^j, Q_2^k, Q_3^l \qquad (12)$$

We are not concerned here with any aspect of this fit; for the present purpose it provides a realistic potential in which to carry out a test of the VSCF method. The "exact" eigenvalues for the same potential were obtained by mixing a reference VSCF state with a large virtual-state basis. As a standard against which to measure the accuracy of the VSCF theory, we also calculated the energies from the NMHO model. Twenty-nine states of energies up to 13000 cm^{-1} above the zero-point energy (4683 cm^{-1}) were calculated.

In Figure 1 we plot the error in the NMHO and VSCF energies vs. the total energy. At a glance, we can see that the VSCF energies are much more accurate than the harmonic ones. Closer examination also reveals that the error in the NMHO energies is growing much more rapidly with energy than the error in the VSCF energies. Some statistics: the average error in the harmonic energies is 538 cm^{-1} whereas for the VSCF energies it is 117 cm^{-1}. These average absolute errors translate into average relative errors of 6.4% for the harmonic oscillator energies and 1.3% for the VSCF energies. Thus, if we consider the difference betwen the NMHO and exact energies as the standard, we see that the VSCF method recovers 80% of the error on the average. The remaining 20% is due to correlation between the vibrational modes. This correlation can only be recovered by doing some mixing of the VSCF and virtual states. For this example then, we conclude that the VSCF method indeed works well.

There are some relatively large isolated errors in the VSCF energies. These are shown very clearly as spikes in Figure 1. These larger errors occur for states in which there is considerable excitation in all of the modes. For example, the spikes at 10316, 11130, and 12487 cm^{-1} occur for the states $|1,2,1\rangle$, $|2,0,1\rangle$, and $|2,1,1\rangle$, where the first, second, and third integer indicates the number of quanta in the symmetric, bending, and asymmetric normal modes. (These state labels are, of course, approximate as the exact states are mixed.) For these states there is substantial mixing between the VSCF states. A very important question then is how much mixing of the VSCF states is necessary to achieve a much more accurate result?

This question was addressed in several studies[12,13] and in a very interesting study by Thompson and Truhlar.[21] They considered a two-mode model for CO_2 in which there is a famous 2:1 Fermi resonance between two quanta of excitation of the bend mode with one quanta of excitation of the asymmetric stretch mode. They explicitly considered these two modes and showed that the VSCF energies of these states were split by only 20% of the exact result. However, by mixing just these two VSCF states, they obtained a splitting equal to 99% of the exact result. Comparable results were also found for other excited Fermi-resonant states. This important study demonstrated that with a minimum amount of mixing the VSCF theory could account for much of the mixing due to Fermi resonances.

Formaldehyde

The next example we wish to consider is formaldehyde, H_2CO. This is a six-mode system and represents the limit of what can be done with CI variational methods. However, it is not a particularly difficult system to study with the VSCF method. We carried out an extensive study of 66 vibrational states of H_2CO and 21 vibrational states of D_2CO using the VSCF and the VSCF-CI methods. These calculations were based on ab initio potential calculated by Harding and fit to a 37-term quartic force field.[30] (The form of the potential is like the one in eq 12 but for six modes.) The objective in that study was to see how well the "exact" VSCF-CI vibrational energies compared with experiment for many transitions. The findings were most satisfying: For the 30 transitions reported experimentally the calculated energies differed on the average by only 11 cm^{-1}. We do not wish to review this study in any detail, rather we wish to point out some of the results of the VSCF calculations and again to contrast the accuracy of this method with those from the NMHO model. In addition, we also consider the uncoupled normal mode anharmonic oscillator model. In this model there is still no coupling between the normal modes; however, the full diagonal part of the potential (the $V_i(Q_i)$) is used. We call this model the uncoupled-anharmonic-oscillator (UAO) model. The energies based on this model, the NMHO model, the VSCF ones, and the "exact" VSCF-CI energies are given in Table I for a number of states, which are labeled by the quantum numbers of the six modes of vibration and the symmetry of each state (H_2CO and D_2CO belong to the C_{2v} point group). The notation $\nu_1\nu_2\nu_3\nu_4\nu_5\nu_6$ indicates the number of quanta in each of the six normal modes which can be approximately characterized according to the following: ν_1, CH symmetric stretch; ν_2, CO stretch;

(29) Bartlett, R. J.; Shavitt, I.; Purvis, G. D., III *J. Chem. Phys.* **1978**, *71*, 281.

(30) Romanowski, H.; Bowman, J. M.; Harding, L. B. *J. Chem. Phys.* *82*, 4155 (1985).

Table I.
Vibrational Energies of H_2CO (in cm^{-1}) from the Normal-Mode-Harmonic-Oscillator (NMHO), Uncoupled-Anharmonic-Oscillator (UAO), Vibrational Self-Consistent-Field (VSCF), and Converged "Exact" (VSCF-CI) Methods

state	sym	NMHO	UAO	VSCF	VSCF-CI
000000	A_1	5864	5880	5796	5777
100000	A_1	8802	8756	8610	8559
010000	A_1	7642	7644	7546	7524
001000	A_1	7408	7424	7303	7277
000100	B_1	7053	7085	6948	6938
000010	B_2	8876	8960	8640	8635
000001	B_2	7134	7162	7045	7023
200000	A_1	11739	11581	11371	11275
110000	A_1	10580	10520	10358	10307
101000	A_1	10346	10301	10082	10048
100100	B_1	9990	9961	9716	9692
100010	B_2	11814	11836	11460	11367
100001	B_2	10071	9842	9825	9784
020000	A_1	9420	9395	9282	9256
011000	A_1	9186	9188	9050	9017
010100	B_1	8831	8849	8690	8676
010010	B_2	10654	10724	10386	10362
010001	B_2	8912	8925	8790	8781

ν_3, CH_2 in-plane bend; ν_4, umbrella motion; ν_5, CH asymmetric stretch; ν_6, in-plane rock.

As seen in Table I the VSCF energies are substantially more accurate than NMHO and the UAO ones. Thus, as in the case of H_2O, the VSCF energies are quite accurate. And as in that case the uncoupled picture is really quite inaccurate even for the fundamental transitions. Some statistics: the average error of the NMHO energies is 223 cm^{-1}, for the UAO energies it is 209 cm^{-1} whereas it is only 33 cm^{-1} for the VSCF energies. Thus in this example, the UAO model is really not a substantial improvement over the NMHO one. Again, if we consider the error between the NMHO energies and the exact ones as the standard, then the VSCF method recovers 85% of that error. Recall that for H_2O 80% of that error was recovered. The VSCF method did slightly better for the six-mode formaldehyde than for the three-mode water! So, based on these two realistic examples along with many model studies,[11-14] we feel it is safe to say that the VSCF method works quite well and that it is substantially more accurate than the NMHO model.

Let's now consider several effective potentials for a state of H_2CO in which the ν_3 and ν_5 modes have one quanta of excitation and the other modes are unexcited. These potentials and the one for mode ν_1 are shown in Figures 2–4 for these modes. Also, we have plotted the UAO potentials for these modes, i.e., $V_1(Q_1)$, $V_2(Q_2)$, and $V_3(Q_3)$. (The normal mode harmonic potentials are just the harmonic approximation to the UAO potentials shown.) The coordinates are the normal mode displacements from equilibrium of the bare potential. It turns out for symmetry reasons that the effective potential for mode 5 must be symmetric about the origin, and so the difference between the effective and UAO potentials for that mode appears to be small. However, for modes 1 and 3 there is no such symmetry restriction, and there are substantial differences between the VSCF effective potentials and the UAO ones.

A Model Two-Mode Isomerization Reaction

In the final example we consider the effect of the rate of isomerization due to excitation of an harmonic mode,

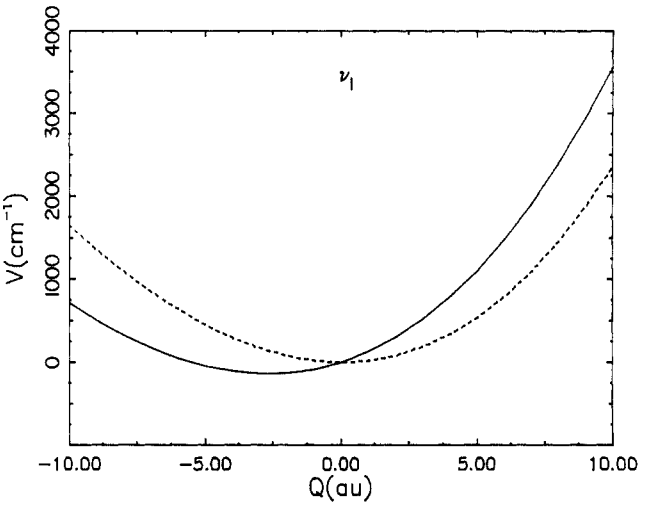

Figure 2. Uncoupled anharmonic (dashed curve) and vibrational self-consistent-field (solid curve) effective potentials for mode 1 of H_2CO.

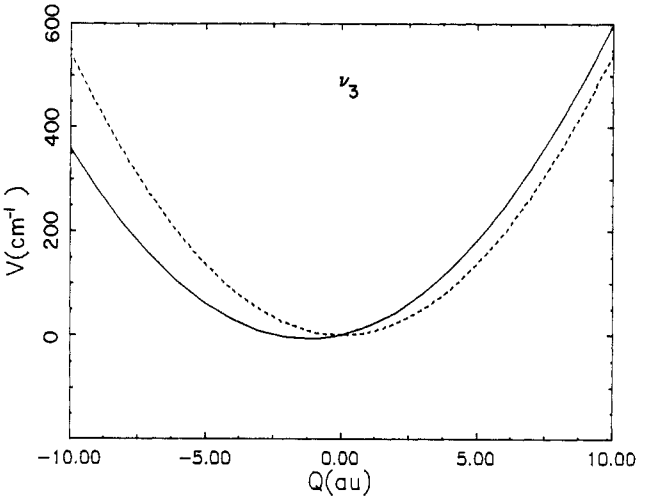

Figure 3. Same as Figure 2 but for mode 3.

which is coupled to the isomerization mode.[31] The potential is given by

$$V(x,y) = V_{dw}(x) + m\omega^2(x)y^2/2 \quad (13)$$

where

$$V_{dw}(x) = ax^2/2 + bx^4/2 + V_0 \exp(-cx^2) \quad (14)$$

and

$$\omega(x) = \omega_0(1 - \lambda \exp(-gx^2)) \quad (15)$$

(The parameter values are given in reference 31). This potential represents a simple physical picture. The potential, $V_{dw}(x)$, is a symmetric double well (the two stable minima represent the two isomers) which is coupled to an harmonic potential in the y degree of freedom. The coupling between these modes is due to the variation of the harmonic frequency along the reaction coordinate, x. The form of the function $\omega(x)$ causes a minimum in the harmonic frequency at the barrier to isomerization. This is a reasonable change of a frequency along a reaction coordinate. The interest here is to examine the rate of isomerization as a function of the degree of excitation of the y-mode. Thus,

(31) Christoffel, K. M.; Bowman, J. M. *J. Chem. Phys.* **1981**, *74*, 5057.

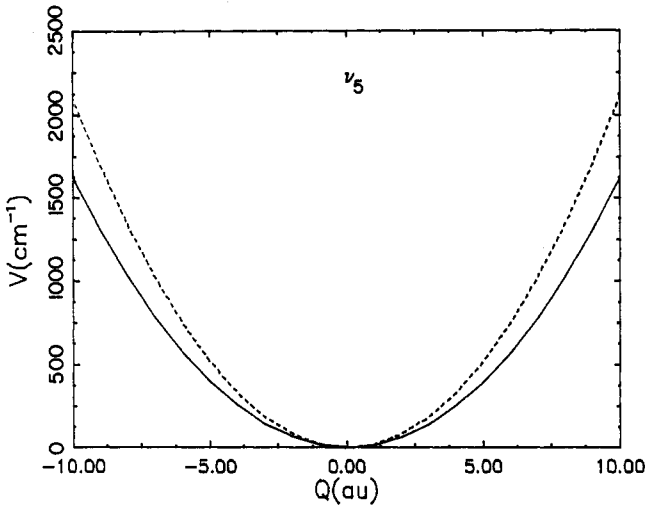

Figure 4. Same as Figure 2 but for mode 5.

Table II
Energy Splittings (in cm^{-1}) for the Coupled Two-Mode Double Well

n_y	Δ_{01}^{VSCF}	$\Delta_{01}^{VSCF-CI}$	Δ_{23}^{VSCF}	$\Delta_{23}^{VSCF-CI}$
0	0.95	0.95	44.2	44.4
1	1.26	1.28	67.6	68.9
2	1.73	1.77	109.0	112.2
3	2.45	2.55	181.9	187.7
4	3.66	3.88	296.9	304.0
5	5.95	6.52	448.2	455.0

we are simulating an experiment in which a chemical reaction, in this case an isomerization, is induced by pumping a mode coupled to the reaction coordinate. In this case it is easy to determine this effect directly from the stationary states of the coupled two-mode system. It is well-known that the rate of a symmetric isomerization is given by[32]

$$k = \Delta/\pi\hbar \tag{16}$$

where Δ is the splitting between pairs of symmetric and asymmetric bound states. Here we will consider the splitting between the energetically lowest and first excited pairs of symmetric and asymmetric bound states. Thus it is necessary to determine the dependence of this splitting on excitation of the harmonic mode. Clearly, to determine this effect the coupling between the x and y modes must be explicitly considered, and thus the NMHO and UAO models are useless for this purpose. We applied the VSCF method to this problem along with the VSCF-CI method, which was used to obtain converged "exact" results. For this two-mode problem we could carry out converged CI calculations. The results are summarized in the Table II. As seen in the VSCF results are in very good agreement with the CI results for both sets of splittings.

The splitting and hence the isomerization rate increases as the harmonic mode is excited, not surprisingly. This means physically that some of the energy deposited into the harmonic mode is made available, through coupling, to the reaction coordinate and thus aids in overcoming the barrier to isomerization. The splitting between the second pair of symmetric and asymmetric bound states is greater than for the first pair. This is due simply to the fact that the barrier to isomerization for excited states is less than it is for the lower energy states, as it should be.

(32) See, for example: Townes, C. H.; Schalow, A. L.; *Microwave Spectroscopy*; McGraw-Hill: New York, 1955; Chapter 12.

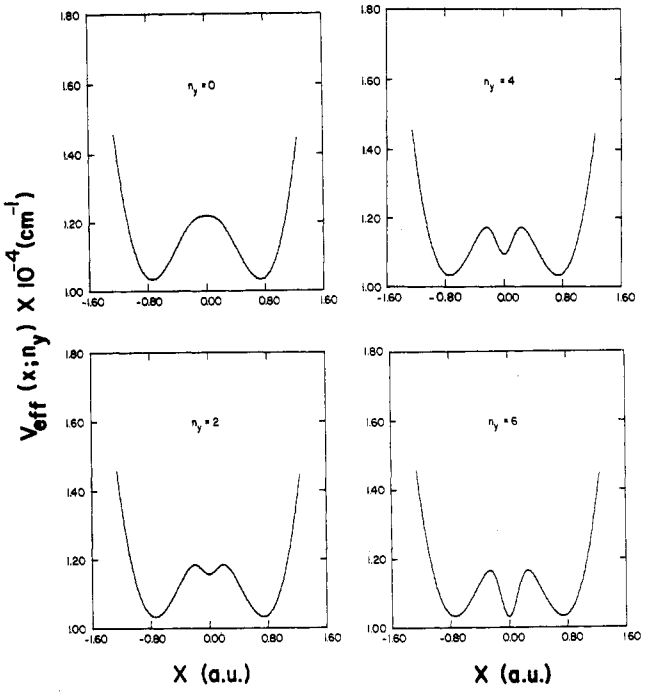

Figure 5. Effective potentials for the reaction coordinate of the coupled double well for the indicated levels of excitation of the harmonic mode transverse to the reaction coordinate.

We now wish to examine several VSCF effective potentials. These can be used to help understand the result that excitation of the harmonic mode does indeed promote the isomerization. Recall that the effective potential for the x-motion is given by $V_{dw}(x)+\langle\phi_{ny}|V_c(x,y)|\phi_{ny}\rangle$ where $\phi_{ny}(y)$ is the VSCF wave function for the harmonic mode and the coupling potential $V_c(x,y)$ equals $m[\omega^2(x) - \omega^2(x = 0)]y^2/2$. The wave function for the y-mode depends of course on the degree of excitation of the x-mode and thus there really is a different effective potential for each pair of quantum numbers n_y, n_x. Four effective potentials for n_x equals zero, i.e., no excitation in the x-mode, are plotted in Figure 5. As seen excitation of the harmonic y-mode produces some dramatic effects on the effective potential. First, the barrier to isomerization decreases, and in fact the single barrier, which is present for $n_y = 0$, splits into two barriers with a "wedge" developing as n_y increases. Thus, the effect of the coupling of the x and y modes not only lowers the barrier to isomerization, it produces a major change in the character of the potential. This change is due to the fact that the frequency of the harmonic mode decreases as x approaches 0. This decrease is quite localized around $x = 0$ and appears as a net decrease in the effective x-potential. In fact, for n_y greater than 7 the wedge that is created in the effective potential is so great that a new bound state is formed exactly where there existed a barrier when n_y equals zero!

This final example is one in which coupling is an essential aspect of the dynamics. Thus, it demonstrates the inherent power of the VSCF method over the NMHO one.

The Future

We anticipate that the VSCF method will be routinely applied to polyatomic systems in conjunction

with electronic structure calculations to determine accurate IR transition energies for fundamental transitions. The method should also prove useful in studying large amplitude motion in large systems such as proteins or van der Waals clusters. For problems in which coupling of modes plays a major role, such as laser-induced isomerization, the method should be especially useful. The question of coordinate system optimization which was just briefly mentioned looks also to be a promising area of future theoretical research.

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