Adiabatic Rotation, Centrifugal Sudden, and Exact Calculations of Rotationally Mediated Fermi Resonances in HOCl†

Shengli Zou, Sergei Skokov,‡ and Joel M. Bowman*

Department of Chemistry and Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta, Georgia 30322

Received: October 13, 2000; In Final Form: January 17, 2001

We investigate rotation-induced Fermi resonances in HOCl by the adiabatic rotation (AR), centrifugal sudden (CS), and exact methods, using a highly accurate potential energy surface [Skokov, S.; Peterson, K. A.; Bowman, J. M. *Chem. Phys. Lett.* **1999**, *312*, 494]. We focus on the rotationally mediated interaction between the (2,3,3) and (3,2,0) (v_{OH},v_{bend},v_{OCl}) states in the $K = 4$ subband using exact, AR, and CS methods. A simple two-state model is used to analyze the interaction, and interaction parameters are determined and compared with those of the experiment. A similar analysis is done for the high-energy interacting pair of states (4,0,0) and (3,2,1), using the AR method, and good agreement with the experiment is found. The comparison between AR calculations and the experiment for the metastable (6,0,0) and (4,4,2) states in the $K = 0$ subband shows good agreement for the value of J where zero-order states cross but not for the coupling constant. We also study rotationally mediated coupling in the pairs of states (1,0,2) and (0,3,2), (1,1,1) and (1,4,1), and (3,0,0) and (2,1,3) using exact and approximate methods. These interactions have not been studied experimentally.

I. Introduction

Hypochlorous acid (HOCl) plays an important role in ozone layer depletion,[1−3] and thus, the spectroscopy in both the ground and electronically excited states has been extensively studied.[4−10] The rovibrational spectroscopy shows readily assignable states; however, strong interactions among several pairs of states have been inferred experimentally. These interactions have been shown to be strongly mediated as a function of the HOCl rotational quantum numbers J and K_a.

Abel and co-workers[6−8] have identified several perturbed spectroscopic features using high-resolution intracavity laser absorption spectroscopy. These authors observed that the $K_a = 4$ rotational subband of the (3,2,0) state (3, 2, and 0 are vibrational quantum number of OH vibration, bending, and OCl vibration, respectively) is significantly perturbed by a dark state, which they assigned as the (2,3,3) state. Similar perturbations for the (4,0,0) state for $K_a = 6$ and 7 subbands have been suggested to be due to the coupling with the (3,2,1) and possibly several other states. Callegari et al.[4] and Dutton et al.[5] studied the coupling between the metastable (6,0,0) and (4,2,2) states in the $K_a = 0$ subband in double-resonance experiments.

Ab initio calculations of these interactions require both a highly accurate potential-energy surface (PES) and a very accurate treatment of vibration/rotation mixing. A first attempt at such calculations was reported recently by Chen et al.[11] This group used a first generation fit to high quality ab initio calculations of the potential,[12] and the rotation−vibration coupling was treated using the centrifugal sudden (CS)[13,14] and adiabatic rotation (AR)[15,16] approximations. These calculations did find that the (3,2,0) state is indeed significantly mixed with the (2,3,3) state near $J = 28$ and $K = 4$ and $J = 14$ and $K = 3$, whereas the (4,0,0) and (3,2,1) states couple at $J = 43$ in the $K_a = 8$ subband. These findings are good qualitative agreement with the experiment. However, quantitative agreement was not obtained because of slight inaccuracies in the PES and perhaps because of slight errors in the methods used to treat rotation−vibration coupling. Also this group did not consider the mixing between the (4,4,2) and (6,0,0) states.

More recently, a new PES has been developed,[17] based on a global ab initio potential,[18] and adjusted using a perturbative inversion technique.[19,20] With this adjustment, the PES reproduces experimental vibrational energies for 22 known bound states for $J = 0$ to within less than 1 cm^{-1} and rotational constants for nine low energy states. The fit to rotational energies was made using the AR approximation. We used this potential in the present new calculations of rotationally mediated Fermi resonances.

The methods used and the details of the calculations are described in the next section. Results and discussion are given in section 3, and a summary and conclusions are given in section 4

II. Method and Calculational Details

The exact rovibrational Hamiltonian for triatomic molecules is well-known.[13,14] For the present purpose, we write it as

$$\hat{H}^J = \hat{H}^{J=0} + \frac{J(J+1) - 2K^2}{2\mu R^2} - \frac{\hat{J}_+\hat{j}_- + \hat{J}_-\hat{j}_+}{2\mu R^2} \qquad (1)$$

where J is the total angular momentum quantum number, R is the distance of an atom from the center of mass of the remaining two atoms, the diatom (in the present case Cl−OH), μ is the corresponding reduced mass, K is the projection quantum

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[†] Part of the special issue “Aron Kuppermann Festschrift”.

[*] To whom correspondence should be addressed. E-mail: bowman@euch4e.chem.emory.edu.

[‡] Present address: Intel Corporation, 2200 Mission College Blvd, Mailstop SC12-205, Santa Clara, California 95052.

10.1021/jp003773i CCC: $20.00

number of J on the body-fixed Z axis (in the present case, the vector **R**), and $\hat{J}_{-/+}$ and $\hat{j}_{-/+}$ are the raising and lowering operators associated with $\hat{J}$ and $\hat{j}$, respectively, in the rotating frame. The potential and kinetic energy operators are contained in $\hat{H}^{J=0}$.

The method we used to obtain the eigenfunctions and eigenvalues of this exact Hamiltonian is based on obtaining eigenfunctions of the widely used approximate Hamiltonian, the CS Hamiltonian, given by[13,14]

$$\hat{H}_{CS}^{J,K} = \hat{H}^{J=0} + \frac{J(J+1) - 2K^2}{2\mu R^2} \tag{2}$$

This Hamiltonian assumes that K is a good quantum number, and it is, in effect, a symmetric-top Hamiltonian, with the top axis coincident with the body-fixed Z axis, which is **R** in the present case. Eigenfunctions and eigenvalues of this approximate Hamiltonian were obtained by doing a number of diagonalizations of smaller one- and two-dimensional reference Hamiltonians, while truncating high energy eigenfunctions at each step, as described in detail elsewhere. The effective two-dimensional Hamiltonian in $r-R$ coordinates, for γ, the usual Jacobi angle, fixed at the equilibrium value, was constructed and diagonalized in a box $2.2 < R < 10$ bohrs and $1.0 < r < 4.0$ bohrs using 3200 direct product basis functions (80 numerical one-dimensional R functions and 40 numerical one-dimensional r functions) to obtain two-dimensional eigenfunctions. These in turn were recoupled with appropriate associated Legendre polynomials to form a three-dimensional basis. For the largest calculation reported here, we recoupled the 150 lowest energy two-dimensional eigenfunctions with 40 associated Legendre polynomials (defined on 60 Gauss–Legendre quadrature points) to obtain 5000 three-dimensional basis functions.

These eigenstates were used as a basis for diagonalization of the full Hamiltonian, which is block-diagonal in the K-quantum number. We were able to calculate well converged eigenvalues of the full Hamiltonian up to excitation energies of 14 000 cm^{-1} above the zero-point energy.

As noted, the CS approximation can be regarded as a symmetric-top approximation in which the top axis is **R**. An alternate approximation is to determine the "instantaneous" principal axis system for a given nuclear configuration and calculate the rotational energy, either by making a symmetric-top approximation in this system or by diagonalizing the asymmetric-top rotor Hamiltonian. The resultant rotational energy is then added to $\hat{H}^{J=0}$ to obtain the AR Hamiltonian[15]

$$\hat{H}_{\text{AR}}^{J,K_a,K_c} = \hat{H}^{J=0} + E^{J}_{K_a,K_c}(R,r,\gamma) \tag{3}$$

In the symmetric-top approximation, K_a is a good quantum number and

$$E^{J}_{K_a}(R,r,\gamma) = \bar{B}(R,r,\gamma)J(J+1) + [A(R,r,\gamma) - \bar{B}(R,r,\gamma)]K_a^{\,2} \tag{4}$$

where $\bar{B}$ is the average of the B and C constants, J is the rotational quantum number, and K_a is the usual projection quantum of $\hat{J}$ on the a axis. The calculation of AR rotation energies follows the procedure described above for the CS calculation, but specific to $J = 0$, with the addition of the rotational energy given by eq 4.

For $J = 0$, the CS and AR Hamiltonians are identical and also exact. The computational effort in doing AR (symmetric-top version) and CS calculations for J and K greater than zero are essentially the same. Each calculation has to be repeated for a given value of J and K_a (K).

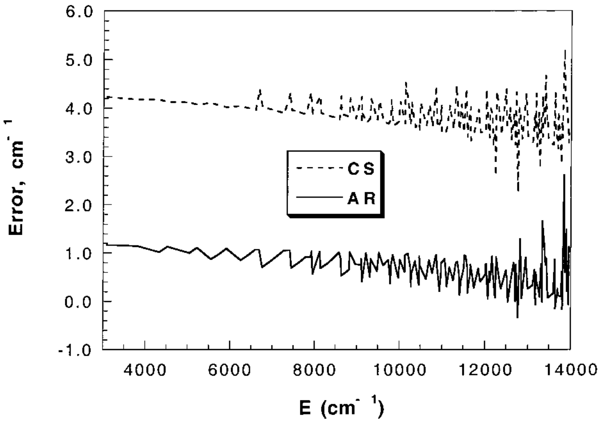

Figure 1. Comparison of CS and AR energies with exact ones for $J = 20$ and $K_a = 1$.

Rovibrational energies of HOCl were obtained using the CS and AR approximations and also exactly for selected values of K_a in order to test these approximations. The eigenvalues and eigenfunctions were used to analyze mixings among vibrational states induced by the rotational motion. A simple physical picture of the origin of this effect is based on the following "zero-order" expression for the rovibrational energy of a vibrational state i

$$\epsilon_i^{J,K} = \epsilon_i^{J=0} + \bar{B}_i J(J+1) + (A_i - \bar{B}_i)K^2 \tag{5}$$

where $\bar{B}_i$ and A_i are the state-specific rotation constants and where for simplicity we drop the subscript "a" in K_a hereafter. This expression can be used to predict the value of J for say a fixed K, where two states cross, in zero order. Of course, states do not cross (except if they are of different rovibrational symmetry), and if we assume that states interact in a pairwise fashion, then in the vicinity of an avoided crossing the difference in the energy of the exact eigenstates can be simply represented (as is done spectroscopically) by

$$\Delta E = \sqrt{4V^2 + \Delta\epsilon^{J,K}} \tag{6}$$

where V is the coupling constant and $\Delta\epsilon^{J,K}$ is the difference in the zero-order energies, given by eq 5. Our approach, guided by experiment, is to fit the rigorous calculated energy difference ΔE by eq 6 and to determine V and $\Delta\epsilon^{J,K}$ from a least-squares fit as described in detail elsewhere.[11] Note, however, that in the fit $\Delta\epsilon^{J,K}$ is written as $\Delta\epsilon^{K} + \Delta\bar{B}_i J(J+1)$, where $\Delta\epsilon^{J,K}(J+1)$ is the difference of the exact eigenvlaues for the given value of K and $J = K$, i.e., the minimum value of J.

III. Results and Discussion

Tests of the CS and AR Approximations. The AR, CS, and exact methods were used to calculate the rovibrational states of the HOCl. The asymmetry parameter of HOCl is very close to one as determined by our calculations and also from the experiment; this indicates that HOCl is a near symmetric-top. (In our calculation, the energy difference between the symmetric and asymmetric method in the energy range of our interest is typically within 0.15 cm^{-1}.) Therefore, we used only a symmetric-top version of the AR method for the calculations reported below. The comparisons between CS and exact energies and between AR and exact energies for $K = 1$ and $J = 20$ are given in Figure 1. Both the AR and CS approximations slightly

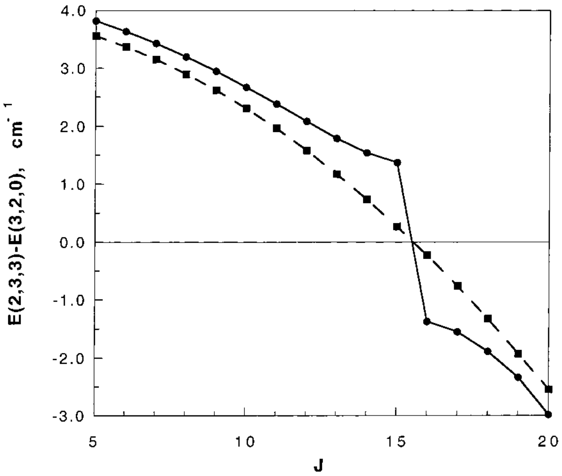

Figure 2. Zero-order (dashed line) and exact coupled (solid line) energy difference for the states (2,3,3) and (3,2,0) vs J for $K_a = 4$.

overestimate rovibrational energies, but the AR energies are more accurate than the CS ones. Note that the CS approximation does depend on the choice of Jacobi coordinates and the body-fixed Z axis. We have made the optimum choice, where $\mathbf{R}$ (the body-fixed Z axis) is the position vector of Cl to the center of mass of OH.

Next we present results of rotationally mediated coupling for pairs of eigenstates. For some of these, the results are based on both exact and approximate calculations, and this will constitute another test of the CS and AR approximations.

The first pair of states we consider are (2,3,3) and (3,2,0). The energies of these states has been observed experimentally for the $K = 4$ subband.[6] We were able to do exact calculations for these states, and the results are shown in Figure 2. Note, we refer the rovibrational energies to a reference rotational energy indicated in the figure to better display the avoided crossing of these two states in the vicinity of $J = 16$. The J dependence of the energies of these two states was fit to eq 6 (the maximum error of the fitting is 0.04 cm^{-1}), and the zero-order energies, determined from the fit and based on eq 5, are also shown. One can clearly see an avoided crossing at $J = 16$. The present calculations show much better agreement with the experimentally observed avoided crossing at $J = 11$[6] as compared to the previous calculation[11] in which the predicted crossing was at $J = 28$. The values of the Fermi coupling constant V and ΔB are also in better agreement with the experiment (Table 1). Note also from Table 1 that the numerically determined constants V and ΔB are in good agreement among all of the calculational methods. Thus, even if the calculated absolute energies are slightly different, the energy differences, which are what are used in determining V and ΔB, may be quite close.

To further examine the coupling of the (2,3,3) and (3,2,0) states, we calculated the dependence of the expectation values of r with J, and the results are shown in Figure 3. At both high and low J, $\langle r \rangle$ values for the (2,3,3) and (3,2,0) states are close to the corresponding values for unperturbed states; however, their values converge to each other as the energy levels become closer, and they are almost same at $J = 15$ and 16. This is an indication that these two states are strongly mixed at these values of J. Also, there are two abrupt changes of $\langle r \rangle$ at $J = 8$ and 20 for the (3,2,0) state; these are caused by the coupling with other states whose energies are only 0.5 cm^{-1} different from the (3,2,0) state at two J values. The strong mixing of (3,2,0) and (2,3,3) states at $J = 16$ and $K = 4$ can also be confirmed by the inspection of the corresponding eigenfunctions. This was done previously,[11] although as noted at $J = 28$, and so, we do not show the figure here.

TABLE 1: ΔB (cm^{-1}) and Coupling Constant V (cm^{-1}) for Fermi Pairs of Interacting States

	calculated		experimental	
Fermi pairs	ΔB	V	ΔB	V
(2,3,3)/(3,2,0)	0.016[a]	0.678[a]	0.015[d]	0.435[d]
	0.015[b]	0.673[b]		
	0.017[c]	0.672[c]		
(4,0,0)/(3,2,1)	0.0074[a]	3.95	$\sim 10^{-4}$[d]	2.99[d]
(6,0,0)/(4,2,2)	0.016[a]	0.44[a]	0.015[e,f]	4.8[e,f]*
(1,0,2)/(0,3,2)	0.0054[a]	2.02[a]		
	0.0040[b]	2.07[b]		
	0.0053[c]	2.06[c]		
(1,1,1)/(1,4,1)	0.0045[a]	0.624[a]		
	0.0038[b]	0.75[b]		
	0.0045[c]	0.71[c]		
(3,0,0)/(2,1,3)	0.015[a]	0.221[a]		
	0.014[b]	0.235[b]		
	0.016[c]	0.226[c]		

[a] AR. [b] Exact. [c] CS. [d] Reference 6. [e] Reference 4. [f] Reference 5.

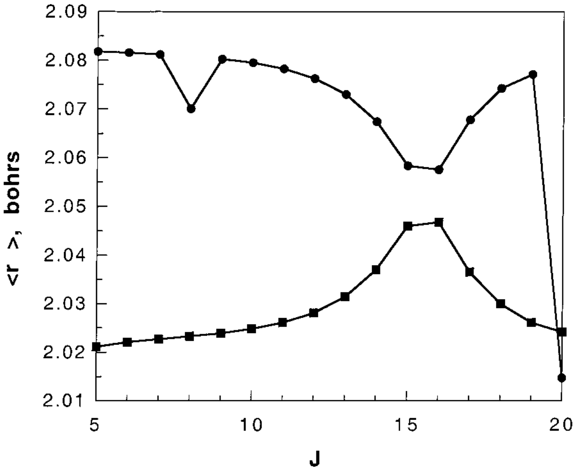

Figure 3. Expectation value of r for the states (3,2,0) (filled circles) and (2,3,3) (filled squares) vs J for $K_a = 4$.

The perturbation of the (4,0,0) state was also studied experimentally for the $K = 8$ subband by Hamman et al.[6] They argued that this state was perturbed by the (3,2,1) state, and this was qualitatively confirmed by the earlier calculations of Chen et al.[11] The energy differences between the (4,0,0) and (3,2,1) eigenstates and corresponding zero-order states for $K = 8$ subband are shown in Figure 4. In this figure, we have plotted the difference in the exact energies as well as the zero-order energies. Not that in this case the zero-order energies approach each other but do not exactly go to zero. Equation 6 was used again to determine V and ΔB (and both given in Table 1). We found a relatively large value of V, 3.95 cm^{-1}, which is in good agreement with the experimental[6] value of 2.99 cm^{-1}.

Recently, Calleagari et al.[4] and Dutton et al.[5] observed that the bright state (6,0,0) is strongly perturbed in the $K = 0$ subband for J in the range of 20−30. The difference in rotational constants of the (6,0,0) and (4,4,2) zero-order states, ΔB, is 0.015 cm^{-1}, and the crossing point occurs at $J = 22$. The experimental and calculated AR energy differences between these two states are plotted at Figure 5. The present calculation gives $\Delta B = 0.016$ cm^{-1} and the crossing point at $J = 28$, in good agreement with experimental value of approximately 22. However, our computed Fermi coupling constant is 0.44 cm^{-1} which is 10 times smaller than the nominal experimental value of 4.8 cm^{-1}.

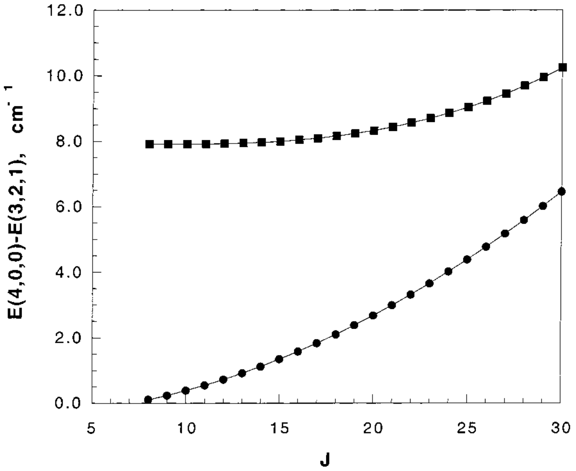

Figure 4. Energy difference between the AR coupled (squares) and zero-order (circles) (4,0,0) and (3,2,1) states vs J for $K_a = 8$.

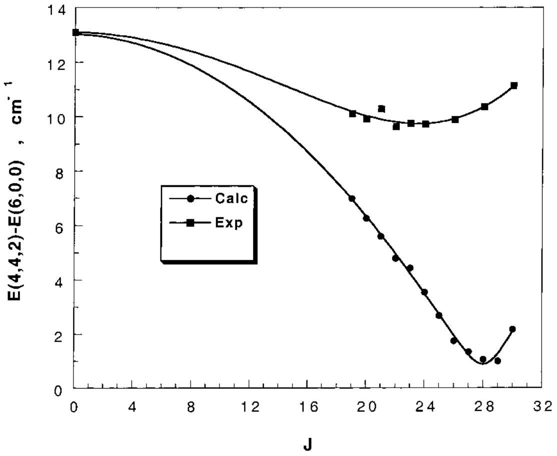

Figure 5. Experimental and AR energy difference between the states (4,4,2) and (6,0,0) vs J for $K_a = 0$.

However, both groups noted that this value is unreasonably large, and it was concluded that additional dark states are involved in interactions with (6,0,0). Thus, the comparison with the experiment is a bit uncertain in this case.

There are, of course, many rotationally induced Fermi interactions. We have examined several others in the $K = 0$ subband, which have not been reported experimentally. The results of these studies are summarized in Table 1, where in all cases exact calculations were done. As seen, there is generally good agreement between the results of the approximate methods and those of the exact ones.

IV. Summary and Conclusions

Using an improved PES, we investigated rotation-induced Fermi resonances in HOCl by the AR, CS, and exact methods. Comparison of AR and CS rovibrational energies for $K = 0$ with the exact results indicate that both methods are quite accurate, with, however, the AR being more accurate than the CS method. The accuracy of these approximate methods is not surprising given that HOCl is a nearly symmetric prolate top.

We studied the rotationally mediated interaction between the (2,3,3) and (3,2,0) states in the $K = 4$ subband using exact, AR, and CS methods. A simple two-state interaction model was used to analyze the interaction. The energies of the zero-order states were predicted to cross point at $J = 16$, in good agreement with the experimental result of $J = 11$. Interaction parameters were also determined and compared favorably with the experiment. The comparison between the exact and approximate methods indicated that both approximation methods are of high accuracy. A similar analysis was done for the high-energy interacting pair of states (4,0,0) and (3,2,1), using the AR method, and again good agreement with the experiment was found. The comparison between AR calculations and the experiment for the metastable (6,0,0) and (4,4,2) states in the $K = 0$ subband showed good agreement for the value of J where zero-order states cross but not for the coupling constant. This may be due to the complication of additional interacting states, inferred experimentally, or small errors in the potential or perhaps small errors in the AR method for these high energy states. We also studied rotationally mediated coupling in the pairs of states (1,0,2) and (0,3,2), (1,1,1) and (1,4,1), and (3,0,0) and (2,1,3), using exact and approximate methods. These interactions have not been studied experimentally.

Acknowledgment. J.M.B. thanks the National Science Foundation (CHE-9873571) for support. We dedicate this paper to Aron Kuppermann.

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