Microwave spectra of $C_2H_4 \cdot H_2O$ and isotopomers

Anne M. Andrews and Robert L. Kuczkowski
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

(Received 26 August 1992; accepted 7 October 1992)

The rotational spectrum of the ethylene-water complex has been reexamined using Fourier-transform microwave spectroscopy. Several new transitions were observed in the spectrum of the normal isotopic species. All the transitions were split into doublets with a 3:1 relative intensity ratio. Additionally, the spectra of $C_2H_4 \cdot HDO$, $C_2H_4 \cdot D_2O$, $C_2H_4 \cdot H_2{}^{18}O$, $C_2H_4 \cdot H_2{}^{17}O$, *cis*-CHD=CHD · H_2O, *trans*-CHD=CHD · H_2O, 1,1-CD_2=$CH_2 \cdot H_2O$, and CHD=$CH_2 \cdot H_2O$ were measured. Splitting patterns and relative intensities of the tunneling doublets of the isotopomers are consistent with a high-barrier tunneling pathway which exchanges the two water hydrogen atoms. A second, low-barrier internal rotation of the water about the hydrogen bond is proposed to explain anomalous dipole moment and ^{17}O nuclear quadrupole coupling results.

I. INTRODUCTION

Because of the importance and abundance of water, there is a great interest in understanding its interactions with other molecules. The spectroscopic characterization of the structures and internal dynamics of weakly bound water complexes has been a valuable resource in this endeavor, yielding information about the biomolecular interactions of water with a large number of binding partners. Particularly, the complexes of water with hydrocarbons, including acetylene,[1] ethylene,[2] benzene,[3] cyclopropane,[3] and propane,[4] have been studied as models of hydrophobic interactions.

The ethylene-water ($C_2H_4 \cdot H_2O$) complex has been the subject of several previous investigations, including *ab initio* calculations, matrix isolation infrared, and molecular-beam electric resonance spectroscopic studies. The *ab initio* calculations, reported by Del Bene in 1974, indicated that the complex would have a structure with the water hydrogen bonded to the C=C bond center as illustrated in Fig. 1, where $\theta_{H_2O}=42°$ and $R_{c.m.}=3.65$ Å.[5] It was found that the binding energy was largely insensitive to rotation of water about the hydrogen bond (coordinate τ in Fig. 1) with a barrier to internal rotation of about 2 cm^{-1}. Further, a bifurcated double-hydrogen-bonded structure with $\theta_{H_2O}=0°$ was found to be only 45 cm^{-1} higher in energy than the singly-hydrogen-bonded structure; this led to the proposition that an inversion-type tunneling motion of the water subunit through the coordinate θ_{H_2O} was also likely. The findings of matrix isolation IR studies are consistent with the hydrogen-bonded structure for the ethylene-water dimer.[6]

The rotational spectrum of the $C_2H_4 \cdot H_2O$ complex was observed by Peterson and Klemperer using the molecular-beam electric resonance technique in 1986.[2] The spectrum was consistent with a hydrogen-bonded structure similar to that predicted by the *ab initio* calculations, with $R_{c.m.}=3.413$ Å, $\theta_{H_2O}=60°$, and $\tau=90°$. Several of the observed transitions for the normal isotopic species were split into doublets, while splittings were not observed in the $C_2H_4 \cdot D_2O$ isotopomer. Assuming that the splittings arose from excited torsional levels resulting from an internal rotation of the water about the τ coordinate, the barrier to this motion was calculated as 353(77) cm^{-1}, considerably higher than expected from the *ab initio* results.

Recently, we have reported on the microwave spectrum, structure, and internal dynamics of the cyclopropane-water complex.[3(c)] It is shown to have a structure like the ethylene-water complex with the water similarly bonded to a CH_2–CH_2 edge as if hydrogen bonding to the pseudo-π system of the cyclopropane. All the rotational transitions were doubled. Based on the study of a large number of isotopomers, the doublets were attributed to an inversion-type motion of the water subunit through a bifurcated, double-hydrogen-bonded intermediate. Furthermore, evidence of anomalies in the dipole moment and ^{17}O nuclear quadrupole coupling constants of the $C_3H_6 \cdot H_2{}^{17}O$ isotopomer indicated that the water was also involved in a nearly free internal rotation about the hydrogen bond.

We suspected that C_2H_4 and C_3H_6 complexes which are structurally alike might exhibit quite similar internal dynamics. In light of this, we decided to reexamine the ethylene-water complex to evaluate whether a hydrogen interchange motion may also be present. Because the Peterson and Klemperer studies were limited to $C_2H_4 \cdot H_2O$ and $C_2H_4 \cdot D_2O$, we have examined the $C_2H_4 \cdot HDO$, $C_2H_4 \cdot H_2{}^{18}O$, $C_2H_4 \cdot H_2{}^{17}O$, *cis*-CHD=CHD · H_2O, *trans*-CHD=CHD · H_2O, 1,1-CD_2=$CH_2 \cdot H_2O$, and CDH=$CH_2 \cdot H_2O$ isotopomers. The results are consistent with internal dynamics for the ethylene-water complex similar to those of the cyclopropane-water complex. The tunneling splittings can be associated with a high-barrier inversion-type tunneling motion through the θ_{H_2O} coordinate with a bifurcated intermediate; additionally there is evidence of a nearly free internal rotation about the τ coordinate.

II. EXPERIMENT

A. Spectrometer

The rotational spectrum of the complex was observed in a Balle–Flygare-type Fourier-transform microwave

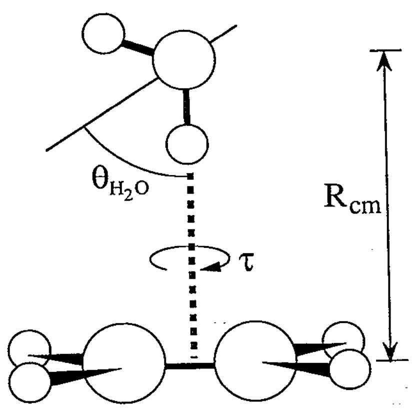

FIG. 1. Structural parameters of the ethylene-water complex. $R_{c.m.}$ is the distance between the centers of mass of the ethylene and the water molecules. θ_{H_2O} is the angle between the C_2 symmetry axis of water and $R_{c.m.}$. τ is the torsional angle between the molecular plane of water and the C=C bond of ethylene (i.e., for $\tau=0°$ the water plane and the C=C bond are coplanar, as drawn, and for $\tau=90°$, they are perpendicular). The oxygen and carbon atoms define the *ab inertial* plane of the complex, with $R_{c.m.}$ and the *a* axis nearly aligned.

spectrometer which has been described previously.[7] Linewidths were typically 20–30 kHz full width at half maximum with partially resolved Doppler doubling. Center frequencies have an estimated accuracy of ±4 kHz. For the measurement of Stark effects, the spectrometer is fitted with two steel mesh plates separated by 30 cm to which up to 10 kV can be applied with opposite polarities. The electric field was calibrated using the $J=1-0$, $M_J=0-0$ transition of OCS.[8]

B. Samples

The spectrum of $C_2H_4 \cdot H_2O$ was observed by placing about 1 mL of de-gassed, de-ionized water in a 1 L glass sample bulb. About 10 Torr of C_2H_4 (Aldrich) and 1.5 atm of argon (Linde) were then added to the bulb. The vapor pressure of water at room temperature was sufficient to produce the spectrum with good signal-to-noise ratio. Because deuterated water often exchanges with incidental water inside the sample introduction line, the spectra of $C_2H_4 \cdot HDO$ and $C_2H_4 \cdot D_2O$ were observed by placing a 75:25 mixture of D_2O (Cambridge Isotope Labs, 99%) and H_2O in a chamber immediately behind the nozzle orifice. A sample containing 1% ethylene in argon at 1.5 atm was passed over this solution. The spectra of *cis*-CHD=CHD·H_2O, *trans*-CHD=CHD·H_2O, 1,1-CD_2=CH_2·H_2O, CDH=CH_2·H_2O, $C_2H_4 \cdot H_2{}^{17}O$, and $C_2H_4 \cdot H_2{}^{18}O$ were produced with the same procedure as the normal isotopic species using commercial samples. No exchange problems were evident between the $H_2{}^{17}O$ or $H_2{}^{18}O$ and water in the sample line. 1,1-CD_2=CH_2 (98%), *trans*-CHD=CHD (98%), *cis*-CHD=CHD (98%), CDH=CH_2 (98%), and $H_2{}^{17}O$ (38%) were purchased from MSD Isotopes. $H_2{}^{18}O$ (97%) was obtained from Cambridge Isotope Labs.

TABLE I. Rotational transitions and spectroscopic constants (MHz) for $C_2H_4 \cdot H_2O$.

Tunneling Label Relative Intensity	*A* 1	*B* 3
1_{01}-0_{00}	7275.604	7274.636[a]
2_{02}-1_{01}	14 545.901	14 543.959[a]
2_{12}-1_{11}	14 172.337	14 170.659
2_{11}-1_{10}	14 915.166[c]	14 912.676[a]
3_{12}-2_{11}		22 364.149[b]
1_{10}-1_{11}	371.409[b]	371.076[b]
2_{11}-2_{12}	1114.326[b]	1113.097[b]
3_{12}-3_{13}	2228.159[b]	2225.724[b]
2_{20}-2_{21}		4.652[b]
3_{21}-3_{22}		23.255[b]
4_{22}-4_{23}		69.688[b]
A	25 960(30)	25 857(3)
B	3823.617(2)	3822.936(4)
C	3452.099(2)	3451.831(3)
D_J		0.0292(3)
D_{JK}	1.697(2)	1.734(3)
d_1	−0.0031(4)	−0.0030(1)
$\Delta\nu_{rms}$	0.011	0.007

[a] These values have been remeasured and are within 10 kHz of the previous measurements reported in Ref. 2.

[b] From Ref. 2.

[c] Previously reported transition at 14 913.047 MHz could not be reproduced, but a second transition was found at this frequency.

III. RESULTS AND ANALYSIS

A. Spectra

The spectrum of $C_2H_4 \cdot H_2O$ was reexamined and several new transitions were observed. The complete set of transitions is listed in Table I, along with a revised set of rotational constants. As noted by Peterson and Klemperer, all the rotational transitions were doubled. The relative intensities of the two states were measured as 1:3 (lower frequency:higher frequency) with an estimated accuracy of ±15% in the manner reported previously.[9] As will be discussed later, the observed relative intensities are consistent with the nuclear-spin statistical weights associated with the exchange of the two water protons. Accordingly, in Table I the weaker transitions are labeled *A*, corresponding to the spatially symmetric tunneling state which Fermi–Dirac statistics pair to the single antisymmetric nuclear-spin function, while the stronger transitions are labeled *B*, corresponding to the antisymmetric tunneling function which is paired to the three symmetric nuclear spin functions. These labels are associated with the "ground" and "excited" torsional state labels in Ref. 2, respectively.

The observed transitions for $C_2H_4 \cdot HDO$, $C_2H_4 \cdot D_2O$, $C_2H_4 \cdot H_2{}^{18}O$, and $C_2H_4 \cdot H_2{}^{17}O$ are shown in Table II. Because the ethylene-water complex is very light and therefore has large rotational constants, only the $J=2$-1 band is observable in the 7–18 GHz range of our spectrometer. The transitions of $C_2H_4 \cdot HDO$ are not doubled, while in $C_2H_4 \cdot D_2O$ the splittings collapse by about 50% and the relative intensities are 2:1 (lower frequency:higher frequency). For $C_2H_4 \cdot H_2{}^{18}O$ and $C_2H_4 \cdot H_2{}^{17}O$, the relative intensities are approximately 3:1 as in the normal isotopic

TABLE II. Rotational transitions and spectroscopic constants (MHz) of $C_2H_4 \cdot HDO$, $C_2H_4 \cdot D_2O$, and $C_2H_4 \cdot H_2{}^{18}O$.

Isotopic Species	$C_2H_4 \cdot HDO$	$C_2H_4 \cdot D_2O$		$C_2H_4 \cdot H_2{}^{18}O$	
Tunneling Label	*A*	*A*	*B*	*A*	*B*
Relative Intensity		2	1	1	3
1_{01}-0_{00}	7233.230	6929.439[a]			
2_{12}-1_{11}	14 093.696	13 521.980	13 521.220	13 376.332	13 375.620
2_{02}-1_{01}	14 461.302	13 854.676[a]	13 853.580	13 709.235	13 708.109
2_{11}-1_{10}	14 825.075	14 180.768[a]	14 179.316	14 036.625	14 035.257
B	3881.033(6)	3631.274(11)	3630.801(45)	3595.366(69)	3595.008(75)
C	3515.563(6)	3301.839(11)	3301.753(45)	3265.219(69)	3265.188(74)

[a] Previously reported in Ref. 2. Reproduced to within 10 kHz.

species. For $C_2H_4 \cdot H_2{}^{17}O$, the nuclear quadrupole coupling constants were determined. The hyperfine structure was treated as a perturbation of the rotational energy levels. For the more intense *B* state nearly all the hyperfine components were observed resulting in $\chi_{aa} = -5.508(6)$, $\chi_{bb} = 3.659(10)$, $\chi_{cc} = 1.850(16)$ MHz. For the weaker *A* state only the strongest hyperfine components were assigned giving $\chi_{aa} = -5.39(3)$, $\chi_{bb} = 3.94(3)$, $\chi_{cc} = 1.45(6)$ MHz. No effort was made to resolve the deuterium hyperfine structure for $C_2H_4 \cdot D_2O$ and $C_2H_4 \cdot HDO$. The $J = 1-0$ transitions, for which this analysis is most propitious, were outside the spectrometer range as noted earlier. Moreover, this hyperfine structure revealed little about the tunneling dynamics in cyclopropane · HDO partly due to the nearly cylindrical symmetry of the quadrupole coupling tensor about the O–D bond in free HDO.

Table III lists the transitions for the isotopomers substituted on the ethylene. In all cases the transitions were doubled with 1:3 relative intensities as observed in the normal isotopic species. The magnitude of the splittings show a complex dependence on the isotopic substitution, with the splitting of the 2_{02}-1_{01} transition decreased by about 40% for $CDH{=}CH_2 \cdot H_2O$, 1,1-$CD_2{=}CH_2 \cdot H_2O$, and *trans*-$CHD{=}CHD \cdot H_2O$, and by about 85% for *cis*-$CHD{=}CHD \cdot H_2O$.

B. Dipole moments

The μ_a dipole moment for the both states unresolved was measured as 1.0943(6) D by Peterson and Klemperer using Stark effects of the $J = 1$, $K_p = 0$, $M_J = 0$-1 and 1_{01}-0_{00}, $M_J = 0$-0 transitions. We have remeasured the dipole moments of the two tunneling states separately. The observed Stark effects ($\Delta M_J = 0$ selection rules) and coefficients calculated from rigid rotor constants are listed in Table IV. The 2_{12}-1_{11}, $M_J = 0$ and 2_{11}-1_{10}, $M_J = 0$ transitions provide sensitivity to the μ_b and μ_c components, respectively. A perturbation-theory least-squares fit results in $\mu_a = 1.102(2)$, $\mu_b = 0.00(5)$, $\mu_c = 0.119(22)$ D for the *A* state and $\mu_a = 1.094(2)$, $\mu_b = 0.00(5)$, and $\mu_c = 0.087(24)$ D for the *B* state (uncertainties 1σ). This suggests a slightly larger dipole moment for the symmetric tunneling state (1.108 D vs 1.097 D).

C. Internal rotation

Peterson and Klemperer determined that the ethylene-water complex had the water hydrogen bonded to the center of the C=C bond with $\tau = 90°$ and $\theta_{H_2O} = 60°$. The dipole moment components and ^{17}O nuclear quadrupole coupling constants that would be expected for this structure along with those observed are shown in Table V. There is a substantial discrepancy in the μ_c dipole component where the predicted value is 1.5 D and the observed is <0.1 D. The χ_{bb} and χ_{cc} quadrupole coupling constants are also anomalous, with the observed values both approximately midway between those predicted for χ_{bb} and χ_{cc}.

A similar but more pronounced discrepancy was observed in these properties for the cyclopropane-water complex where the measured values were $\mu_b \approx \mu_c \approx 0$ D and $\chi_{bb} \approx \chi_{cc}$. This was proposed to arise from a nearly free internal rotation of the water subunit about the hydrogen bond which averaged the perpendicular dipole moment components and nuclear quadrupole coupling constants.

TABLE III. Rotational transitions and spectroscopic constants (MHz) of $CHD{=}CH_2 \cdot H_2O$, 1,1-$CH_2{=}CD_2 \cdot H_2O$, *trans*-$CHD{=}CHD \cdot H_2O$ and *cis*-$CHD{=}CHD \cdot H_2O$.

Isotopic Species	$CHD{=}CH_2 \cdot H_2O$		1,1-$CH_2{=}CD_2 \cdot H_2O$		*trans*=$CHD{=}CHD \cdot H_2O$		*cis*-$CHD{=}CHD \cdot H_2O$	
State	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Intensity	1	3	1	3	1	3	1	3
2_{02}-1_{01}	14 269.187	14 268.005	13 994.757	13 993.646	13 994.950	13 993.832	14 019.419	14 019.174
2_{12}-1_{11}	13 889.187	13 888.221	13 623.871	13 622.951	13 598.186	13 597.125	13 639.554	13 639.630
2_{11}-1_{10}	14 645.515	13 463.841	14 362.298	14 360.936	14 388.247	14 386.543	14 397.203	14 397.135
B	3759.6(3)	3759.2(3)	3686.6(4)	3686.3(4)	3699.6(7)	3699.2(7)	3697.8(3)	3697.8(2)
C	3381.5(3)	3381.4(3)	3317.5(4)	3317.4(4)	3304.7(7)	3304.6(7)	3319.0(3)	3319.0(2)

TABLE IV. Stark effects and coefficients for the B state from rigid rotor rotational constants.

Transition		Coefficients A^a	Coefficients B^a	$\lvert M_J \rvert$	Stark effect[b]
1_{01}-0_{00}	a	0.186×10^{-4}	-0.221×10^{-4}	0	0.222×10^{-4}
	b	0.148×10^{-5}	-0.536×10^{-5}		
	c	0.149×10^{-5}	-0.538×10^{-5}		
2_{02}-1_{01}	a	-0.531×10^{-5}	0.962×10^{-5}	0	-0.643×10^{-5}
	b	-0.193×10^{-5}	0.225×10^{-5}	1	0.523×10^{-5}
	c	-0.169×10^{-5}	0.218×10^{-5}		
2_{12}-1_{11}	a	0.443×10^{-5}	0.163×10^{-3}	0	0.543×10^{-5}
	b	-0.167×10^{-3}	0.211×10^{-4}		
	c	0.216×10^{-6}	-0.211×10^{-5}		
2_{11}-1_{10}	a	0.421×10^{-5}	-0.166×10^{-3}	0	0.516×10^{-5}
	b	0.214×10^{-6}	-0.213×10^{-5}		
	c	0.180×10^{-4}	0.441×10^{-6}		

[a] Coefficients from perturbation expression $\Delta\nu=(A+Bm^2)\mu^2E^2$ calculated using rotational constants in Table I.

[b] Measured Stark effects in MHz cm^2 V^{-2}.

The same interpretation is applicable to the ethylene-water results. This is also consistent with the *ab initio* calculation which found that the stabilization energy of the complex was relatively insensitive to the orientation of the water about the hydrogen bond and the barrier to internal rotation through the τ pathway was about 2 cm^{-1}.

The observation that μ_c is not identically equal to zero while μ_b is zero within the measurement uncertainty indicates that the equilibrium structure of the complex has the plane of the water perpendicular to the C=C bond (i.e., has an *ac* symmetry plane) as proposed in the work of Peterson and Klemperer. Also from this information and the observation that the difference between χ_{bb} and χ_{cc} is larger for ethylene-water, one can speculate that the barrier for this pathway, while low, may be higher for the ethylene-water complex than for the cyclopropane-water complex, where the averaging seems to be more nearly cylindrically symmetric.

D. Tunneling doublets

We now address the origin of the doublets observed in the spectrum and whether they arise from the internal rotation discussed earlier or from a different process not yet considered. There are several observations which indicate that the doubling is not simply due to the internal rotation about the hydrogen bond. First, the absence of any first-order Stark effect in either of the tunneling doublets implies that they do not originate from $m=0$ and $m=\pm1$ free internal rotation states; the nearly identical second-order Stark effects for the two states are more indicative of a tunneling process hindered by a barrier. Second, the averaging of the dipole components and quadrupole coupling constants eliminate the possibility of a high-barrier hindered rotation about the hydrogen bond. Finally, the lack of splitting in the $C_2H_4 \cdot HDO$ isotopomer (which has the deuterium in the hydrogen bond) is inconsistent with the doublets arising from either a high- or low-barrier tunneling about the hydrogen bond, but rather suggests a pathway which exchanges the two water hydrogens and which is quenched by asymmetric isotopic substitution.

TABLE V. Dipole moment components and ^{17}O nuclear quadrupole coupling constants predicted from the structure and experimental values.

	Predicted[a] (Rigid)	A state Obs.	B state Obs.
μ_a (D)	1.15	1.101(2)	1.094(2)
μ_c (D)	1.45	0.119(22)	0.087(24)
χ_{aa} (MHz)	-6.039	$-5.39(3)$	$-5.508(6)$
χ_{bb} (MHz)	-4.129	3.94(3)	3.659(10)
χ_{cc} (MHz)	10.169	1.45(6)	1.850(16)

[a] Predicted for a rigid molecule with structure as determined from moments of inertia.

The isotopic data are consistent with a second high-barrier tunneling motion which exchanges the two water hydrogens as the cause of the tunneling doublets. The 1:3 relative intensities of the doublets in the normal isotopic species are consistent with the spin statistical weights arising from the exchange of two protons. Upon deuterium substitution in the $C_2H_4 \cdot D_2O$ the relative intensities change to 2:1, as would be expected for the exchange of two deuterons. Furthermore, the lack of doubling in the $C_2H_4 \cdot HDO$ species supports this idea, as the water hydrogens are in inequivalent positions in the molecule; tunneling splittings would by quenched because the exchange of a proton and a deuteron would result in an inequivalent structure. Finally, deuterium substitution at any position on the ethylene does not affect the relative intensities of the doublets, indicating that the ethylene protons are not exchanged in the tunneling process. It should be remarked that there should be a second isomer for $C_2H_4 \cdot HDO$, with the hydrogen atom in the hydrogen bond and a free deuterium. It is common in weak complexes that this isomer has a higher energy due to zero-point vibrational effects and is usually not seen; no systematic effort was made to search for this form.

With the permutation of the nuclei which are responsible for the doubling of the rotational transitions known, it is interesting to speculate on the pathway which gives rise to this permutation. There are two pathways which present themselves as likely candidates for exchanging the hydrogen atoms on the water. The first is a straightforward rotation of the water subunit about its C_2 axis. The second is a wagging-type inversion motion through the θ_{H_2O} coordinate which is coupled to the low-barrier rotation of the water about the hydrogen bond. Both pathways result in the exchange of the water hydrogens. Several factors favor the choice of the inversionlike motion. The first is the larger value for the μ_a dipole moment for the symmetric tunneling state. As pointed out by Yaron *et al.*,[10] regarding the H_2O–CO complex, this favors the inversion-type pathway. For rotation of the water about the hydrogen bond, no effect on the magnitude of μ_a is expected because the projection of μ_a on the principal axis system remains the same throughout the pathway. However, for the inversion-type motion the μ_a dipole component changes during the tunneling process. Because the symmetric tunneling wave function has a small value at the top of the barrier while the antisymmetric function has a node, a pathway which maximizes the a-dipole moment at the top of the barrier is indicated. This is consistent with an inversion-type motion with a bifurcated intermediate where the entire dipole moment of the water is aligned with the a principal axis at the barrier. A similar difference in μ_a for the two tunneling states was observed for the cyclopropane-water complex.

Since the observed difference in the μ_a components is small and marginally significant given the experimental uncertainties, this rationalization is not entirely compelling. Other factors such as complications from the vibration-rotation interactions associated with the nearly free internal rotation and different effective principal axes for the two states could play a role in the small observed differences in dipole components. These considerations aside, the inversion-type pathway is appealing because it proceeds via a comparatively favorable double-hydrogen-bonded intermediate and allows the hydrogen-bond connection to remain more intact than rotation about the C_2 axis.

Finally, this pathway is described as a coupled inversionlike motion of the water and internal rotation of the water about the hydrogen bond. However, this language is chosen for descriptive convenience. The low-barrier rotation about the hydrogen bond might also be described as the rotation of the ethylene about the hydrogen bond or a geared type rotation of both the water and the ethylene against one another. A coupled pathway involving some ethylene motion would explain the complex dependence of the tunneling splittings on isotopic substitution on the ethylene and the water. A more quantitative analysis of the mechanics of the tunneling motion is beyond the scope of this study.

IV. DISCUSSION

By studying the effects of isotopic substitution on the spectrum of ethylene-water complex, we have been able to shed additional light on the internal dynamics of this complex, which are apparently more complex than initially thought. The ethylene-water complex shows great similarity to the cyclopropane-water complex, both in structure and internal dynamics. Both complexes have the water hydrogen bonded to the π or pseudo-π system of their respective C–C bonds. The spectra of the two complexes exhibit nearly identical properties with regard to the doubling of the rotational transitions, the relative intensities of the doublets and how they are affected by isotopic substitution. Additionally, observations about the dipole moment and nuclear quadrupole coupling constant anomalies and small differences in the dipole moment measurement for the two tunneling states are similar for the two systems, implying that the pathways for the internal motions of the complexes are similar. The doublets observed for each rotational transition are attributed to a high-barrier tunneling motion involving the exchange of the two water protons. Additionally, there is evidence that the complex undergoes a low-barrier internal rotation of the moieties about the hydrogen bond. Excited torsional states from this motion are not observed apparently because in the low temperature of the supersonic expansion all the molecules relax into the A and B tunneling states of the ground torsional state. Efforts to populate these states by employing a lighter, nonrelaxing buffer gas were not attempted. This view of the ethylene-water complex is consistent with the predictions of an *ab initio* study reported nearly two decades ago.

ACKNOWLEDGMENTS

We acknowledge Professor W. Klemperer for comments regarding the interpretation of our cyclopropane-water data which have played a role in this study as well. Helpful discussions with Dr. Amine Taleb-Bendiab are also acknowledged. The research was supported by the Experimental Physical Chemistry Program, National Science Foundation.

[1] K. I. Peterson and W. Klemperer, J. Chem. Phys. **81**, 3842 (1984).

[2] K. I. Peterson and W. Klemperer, J. Chem. Phys. **85**, 725 (1986).

[3] (a) S. Suzuki, P. G. Green, R. E. Bumgarner, S. Dasgupta, W. A. Goddard III, and G. A. Blake, Science **257**, 942 (1993); (b) A. J. Gotch and T. S. Zwier, J. Chem. Phys. **96**, 3388 (1992); (c) A. M. Andrews, K. W. Hillig II, and R. L. Kuczkowski, J. Am. Chem. Soc. **114**, 6765 (1992).

[4] D. W. Steyert, R. D. Suenram, F. J. Lovas, and R. J. Saykally, Ohio State University, International Symposium on Molecular Spectroscopy, Report No. RB04, 1992 (unpublished).

[5] J. E. Del Bene, Chem. Phys. Lett. **24**, 203 (1974).

[6] A. Engdahl and B. Nelander, Chem. Phys. Lett. **113**, 49 (1985); A Engdahl and B. Nelander, J. Phys. Chem. **90**, 4982 (1986).

[7] T. J. Balle and W. H. Flygare, Rev. Sci. Instrum. **52**, 33 (1981); K. W. Hillig II, J. Matos, A. Scioly, and R. L. Kuczkowski, Chem. Phys. Lett. **133**, 359 (1987).

[8] K. Tanaka, H. Ito, K. Harada, and T. Tanaka, J. Phys. Chem. **80**, 5893 (1984).

[9] A. M. Andrews, A. Taleb-Bendiab, M. S. LaBarge, K. W. Hillig II, and R. L. Kuczkowski, J. Chem. Phys. **93**, 7030 (1990).

[10] D. Yaron, K. I. Peterson, D. Zolandz, W. Klemperer, F. J. Lovas, and R. D. Suenram, J. Chem. Phys. **92**, 7095 (1990).