Detection of a Higher Energy Conformer of 2-Phenylethanol by Millimeter-Wave Spectroscopy

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We have detected a second conformer of 2-phenylethanol and determined its shape using Stark-modulated free jet microwave spectroscopy with an elevated preexpansion temperature of 300 °C. By comparison of observed and ab initio predicted spectroscopic rotational constants and hydroxyl-deuteration isotopic substitution coordinates the species has been identified with the C_s trans conformer, designated as **5**. This is in agreement with the previously published results from pulsed-jet UV−IR laser spectroscopy. These workers identified **5** together with the lower energy conformer **1** that also was detected by us in an earlier microwave study. Stark effect measurements on **5** yielded electric dipole moment values of $\mu_a = 0.3282(6)$ D, $\mu_b = 0.0$ D (assumed), $\mu_c = 1.33(7)$ D, and hence $\mu_{total} = 1.37(7)$ D. Previously published large-basis MP2 level ab initio calculations predicted that, because of conformational relaxation, just two conformers should be present following argon jet cooling. However, the C_1 trans conformer **4** was predicted to be more stable than **5**. New ab initio calculations which include radially diffuse basis functions at the MP2/6-311++G(d,p) level now indicate that **5** is more stable than **4**.

Introduction

The structure of the 1,2-disubstituted ethane, 2-phenylethanol, as the oxygen analogue of the neurohormone 2-phenylethylamine (PEA), is of particular interest in the context of gaining improved insights into structure-dependent biological activity. Murcko and DiPaola, who reported ab initio calculations on ethylene glycol and 1,2-dimethoxyethane,[1] reviewed experimental and theoretical evidence for various 1,2-disubstituted ethanes. They concluded that usually the trans orientation of the X−C−C−Y fragment is energetically preferred, although sometimes the gauche conformer is of virtually the same energy and, occasionally (e.g., 1,2-difluoroethane), is of lower energy. They pointed out that a gauche preference may result from intramolecular hydrogen bonding.

For flexible molecules such as these disubstituted ethanes, the possibility exists that more than one conformer is energetically accessible. A previous millimeter microwave spectroscopy study of PEA[2] indicated that two conformers were detectable in the sample vaporized at 400 K. In contrast only a single conformer was detected in a similar millimeter microwave spectroscopy study of 2-phenylethanol.[3]

The most stable conformers of 1,2-disubstituted ethanes such as PEA (involving the benzene ring), histamine[4] (involving the imidazole ring), and 2-vinylethanol[5] (involving the vinyl group) appear to be stabilized by a nonclassical hydrogen bond. This bond forms via an interaction between a hydrogen in the amino or hydroxyl substituent group and the π-electron cloud of the other substituent. Where the amino group is involved, two distinct conformers involving such bonds are possible, but for hydroxyethanes such as 2-vinylethanol and 2-phenylethanol, only one such H-bond-stabilized conformer is anticipated. Therefore it is not surprising that the first reported microwave spectroscopy studies of these compounds[6,3] identified just one conformer in the vapor phase, whereas multiple conformers were detected for the aminoethanes PEA[2] and histamine.[4]

Structural studies of jet-cooled PEA and 2-phenylethanol vapor via LIF and R2PI electronic spectroscopy recently have been reported.[7] Unlike the microwave studies, which involved similar jet physical conditions, the presence of five conformers for both PEA and 2-phenylethanol was deduced via analysis of fine structure in the laser spectra. In a subsequent study utilizing IR−UV double resonance,[8] it was recognized that several of the apparently distinct bands in the UV spectrum of 2-phenylethanol arose from a common electronic ground S_0 electronic state. The splitting between these bands was deduced to arise from previously unanticipated tunnelling splittings in the excited S_1 electronic state for the conformers involved. In light of this analysis it was deduced that the laser spectrum indicated the presence of just two conformers, designated in the notation of these authors as Ggπ and At (and equivalent in the notation of our own previous study[3] to **1** and **5**, respectively).

Large basis ab initio calculations have been reported for 2-phenylethanol in association with the previously published laser spectroscopy studies[7,8] at the MP2/6-311G(d,p) level and at the MP2/6-31G(d,p) level with our earlier microwave spectroscopy work.[3] In both cases it was predicted that conformer **5** was of higher energy than **4**, although the difference fell from 1 to 0.5 kJ mol^{-1} when allowance was made for zero point energy.[3] Overall, the five possible distinct conformers are seen to fall into two groups **1**, **2**, **3** and **4**, **5**, within which the interconformational energy barriers are relatively small (ca. 500 cm^{-1}), but between which the interconformational barriers are large (1500 cm^{-1} or more). For the species of C_1 symmetry, **1**, **2**, **3**, and **4**, each conformer exists as an enantiomeric pair. Where the barrier to interconversion between conformers is less than a critical value (shown to be ca. 800 cm^{-1} for argon expansions entraining target molecules of similar size and polarity[9,4b]), the higher energy conformers will relax to the adjacent lower energy conformer. Therefore it follows that, on the basis of the ab initio calculations, it would be anticipated

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that only two conformers, **1** and **4**, would be expected to be found in the postexpansion jet.

In contrast to this prediction, the previous microwave study found just one conformer (**1**), while the laser spectroscopy study found two conformers (**1** and **5**), rather than **1** and **4**. In this new study we will attempt to reconcile these discrepancies by undertaking further ab initio calculations and a more sensitive microwave spectroscopy search.

Methodology

Experimental Details. The free-jet expansion, Stark-modulated spectrometer used in the present study is identical to that used in the previously reported study[3] and is based on a design that has previously been described.[10] Liquid 2-phenylethanol (99%), obtained from Aldrich and used without further purification, was vaporized at a temperature of 300 °C in a stream of argon at a pressure of ca. 30 kPa. Following free-jet expansion the rotational temperature was found to be ca. 5 K under the conditions employed. O-deuterated 2-phenylethanol was prepared by shaking 2-phenylethanol with acidified D_2O: $H_2O = 1:1$ for 5 min, making it slightly alkaline and separating the organic layer.

The microwave absorption spectrum was first investigated via an extended spectral search scan over a relatively wide frequency range (48−64 GHz). In these strip-chart recorded wide searches the preexpansion temperature was 300 °C, in contrast to the 90 °C employed in the previous study. Once located via the wide search scan, each detected line was digitally acquired via repetitively averaged narrow-band scans, and line frequencies were measured by least-squares fitting of a Lorentzian function to each line profile.

The 33-kHz square-wave Stark modulation system employed parallel-plate electrodes with a separation of ca. 3.5 cm. The square wave modulation field was established by opposed-polarity equal-amplitude ground-clamped voltage waveforms applied to the opposing electrodes. For dipole moment measurements the various M_J lobes for selected transitions were scanned and digitally acquired and the Stark frequency shift was measured by least-squares fitting of a Lorentzian line shape profile. The preset Stark voltages were measured via a precision a/d converter. The effective electrode spacing, which includes allowance for any scale factor error in the voltage measurement, was calibrated from a series of Stark shift measurements on SO_2 for which a precise dipole moment has been determined via molecular beam electric resonance.[11]

Theory. Predictive ab initio calculations of molecular structure, conformational energy, and electric dipole moments at levels up to MP2/6-31G(d,p) were reported in our previous study[3] and at the MP2/6-311G(d,p) level in the laser spectroscopy studies.[7,8] In an attempt to resolve the apparent discrepancy between these predictions of **4** as the second species (after **1**) rather than **5**, which was identified via laser spectroscopy,[8] we undertook new ab initio calculations. These employed the radially diffuse MP2/6-311++G(d,p) level that we have found in previous studies to reconcile discrepancies between experimental jet spectroscopy results and less elaborate ab initio calculations.[4b] These calculations were performed by using the GAUSSIAN 94 package.[12] As with our previous study, the inclusion of vibrational zero-point energy was made from the results of ab initio harmonic approximation vibrational frequency calculations at the MP2/6-31G(d,p) level.

Results and Discussion

Identification. We observed a total of 56 lines (all of μ_c-type) in the frequency range 48−64 GHz that were not attributable to the previously identified species **1**. We were able to assign these to an asymmetric rotor spectrum. Table 1 lists the spectroscopic constants (I^R representation, *S* reduction[13]) derived by a least-squares fit to these lines. A full listing of the observed transitions and the least-squares fit residuals is given in Table 1S. Similarly are listed in Table 1 the spectroscopic parameters derived from the measurement of 47 lines assigned to the O-deutero isotopomer of the same species for which the full listing of observed transitions is given in Table 2S.

TABLE 1: Experimentally Derived Rotational and Centrifugal Distortion Constants[a] for the Newly Observed Conformer y of 2-Phenylethanol and for the Corresponding O-Deutero Isotopomer

	normal isotopomer	O-deutero species
A/MHz	4433.0492(47)	4400.1763(76)
B/MHz	855.4396(25)	830.1132(49)
C/MHz	765.6247(28)	746.1960(52)
D_J/kHz	0.0550(26)	0.0476(38)
D_{JK}/kHz	1.8175(90)	1.752(24)
D_K/kHz	0.827(55)	1.230(81)
d_2/kHz	0.00195(47)	0.00238(14)
no. of lines in fit	56[b]	47[b]
rms residual/MHz	0.057	0.053

[a] The numbers in parenthesis are one standard deviation in units of the least significant quoted digit. [b] Observed frequencies, assigned quantum numbers, and residuals from the fitting calculations are listed in Tables 1S and 2S.

TABLE 2: Experimentally Derived Principal Axis Dipole Moment Components for the Newly Observed Conformer y of 2-Phenylethanol[a]

μ_a/D	0.3282(6)
μ_b/D	0.0 (assumed)
μ_c/D	1.33(7)
μ_{total}/D	1.37(7)
no. of transitions	4
no. of Stark shift measurements	80
rms residual/MHz	0.51

[a] The numbers in parenthesis are one standard deviation in units of the least significant quoted digit. Stark shifts at a series of voltages were measured for the transitions $6_{6,0}-5_{5,0}$; $6_{6,1}-5_{5,1}$; $8_{7,1}-7_{6,1}$, and $8_{7,2}-7_{6,2}$. Voltages, observed Stark shifts, M_J quantum numbers, and residuals from the dipole moment fitting calculation and from the Stark electrode spacing calibration are detailed in Tables 3S and 4S, respectively.

Principal axis dipole moment component values were determined from the analysis of Stark effect measurements on the $M_J = 1,2,3,4,5,6$ lobes of the prolate-degenerate paired μ_c-type transitions $\{6_{60} - 5_{50}; 6_{61} - 5_{51}\}$ and $\{8_{71} - 7_{61}; 8_{72} - 7_{62}\}$. In light of the identification of the species involved as **5** which has C_s symmetry (see below), μ_b was constrained to zero during the least-squares fitting of the dipole moment components. The resulting best-fit dipole moment component values are listed in Table 2. The details of the 80 individual Stark shift measurements and the fit residuals are listed in Table 3S.

The predicted ab initio structures of the five distinct conformers of 2-phenylethanol are shown, together with the nomenclature adopted in this work, in Figure 1. The MP2/6-311++G(d,p) relative energies are listed in Table 3, which also gives relative energies including vibrational zero-point energy, theoretical Gibbs energies at 573 K, and predicted conformer abundance ratio (to be discussed later). As with less elaborate ab initio calculations previously reported,[3,8] the most stable species is predicted to be the gauche conformer **1**. As was shown in our previous study[3] the other gauche conformers—**2** and **3**—are separated from **1** by sufficiently low energy barriers to permit relaxation to **1** during the argon jet expansion. In constrast to

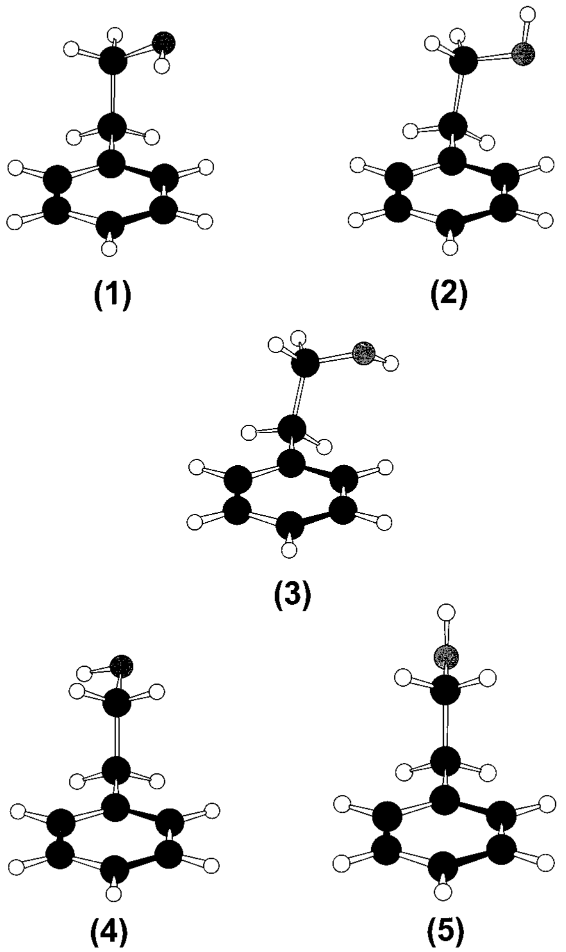

Figure 1. Theoretically predicted structures from ab initio MP2/6-311++G(d,p) calculations of the stable conformers of 2-phenylethanol.

TABLE 3: Predicted Relative ab Initio Energies and Abundances for the Conformers of 2-Phenylethanol Optimized at the MP2/6-311++G(d,p) Level

species	ΔE_{MP2} kJ mol^{-1}	ΔE_{MP2} + ZPE[a] kJ mol^{-1}	$\Delta G_{573\ K}$,[a] kJ mol^{-1}	rel abundance[b] preexpansion at $T = 573$ K	rel abundance[b] postexpansion from $T = 573$ K
1	0.00	0.00	0.00	2.00	1.6
2	7.24	5.93	2.71	1.13	
3	9.91	9.01	5.05	0.69	
4	6.91	5.93	1.83	1.36	
5	6.46	5.01	0.08	0.98	1.0

[a] The vibrational zero-point and thermal Gibbs energy contributions are predicted from Gaussian 94 harmonic force field calculations performed at the MP2/6-31G(d,p) level. The thermal Gibbs energy contribution is for a single enantiomer. [b] Calculated from the theoretical relative Gibbs energies and summed over enantiomers. See discussion in text for details.

previous calculations, with this more elaborate basis set **5** is found to be of lower energy than **4** (by ca. 0.9 kJ mol^{-1}).

The spectroscopic constants predicted from the MP2/6-311++G(d,p) ab initio optimized structures for these conformers are listed in Table 4. These are shown in comparison with the fitted rotational constants for the two detected species, designated **x** and **y**. It is seen that the rotational constants observed for previously detected species **x** are in best agreement with those predicted for the species **1**, **2**, or **3**. The new detected species **y** has rotational constants consistent with those of either of the two trans conformers, **4** and **5**. Therefore **y** cannot be identified on the basis of rotational constants alone.

TABLE 4: Predicted Spectroscopic Parameters from ab Initio MP2/6-311++G(d,p) Calculations

parameter[a]	2-phenylethanol conformer **1**	**2**	**3**	**4**	**5**	obsd **x**	obsd **y**
ΔE_{MP2}/kJ mol^{-1}	0	8.29	9.58	7.78	8.80		
A/MHz	3292.2	3427.3	3326.0	4337.0	4366.0	3338.0	4433.0
B/MHz	1091.3	1084.6	1064.5	857.2	859.4	1083.5	855.4
C/MHz	977.4	919.4	949.8	767.8	770.0	958.9	765.6
rms(O−C)**y**[b]	684	602	659	55	39		
μ_a/D	1.4	1.3	0.6	1.2	0.5	1.25	0.33
μ_b/D	1.2	1.1	0.2	1.3	0.0		0.0[c]
μ_c/D	0.7	1.0	1.8	0.6	1.6		1.33
μ_{tot}/D	2.0	2.0	1.9	1.8	1.7	1.67	1.37

[a] A complete listing of ab initio predicted geometric parameters is given in Table 5S. [b] Root mean square deviation in megahertz between the observed and ab initio rotational constants. [c] The value of μ_b was constrained to zero in the dipole moment fitting calculation.

TABLE 5: Principal Axis Coordinates of the Hydroxyl H Atom for the Conformers of 2-Phenylethanol Predicted at the MP2/6-311++G(d,p) Level Shown in Comparison with the Corresponding Values Obtained from the Application of Kraitchman's Equations to the Experimental Moments of Inertia Found for the Normal and OD Isotopomers of the Newly Observed Species y

species	$\|a\|$ pm	$\|b\|$ pm	$\|c\|$ pm
1	150	93	120
2	308	112	129
3	275	145	37
4	386	73	20
5	412	0	101
obsd[a]	415	8	94

[a] Calculated via Kraitchman's equations from the rotational constant values for the observed species and its O-deutero isotopomer as listed in Table 1.

The measured electric dipole moment components are also listed for comparison in Table 4. As in our previous study this information is not decisive in the identification of **x** as **1**, although it clearly eliminates **x** as **5**. However for species **y**, the small fitted value of μ_a provides strong evidence that this indeed is conformer **5**, since this is the only conformer predicted to have a μ_a value significantly less than 1 D.

As further confirmation of the identity of conformer **y** we considered the assigned O-deutero species. The substitution coordinates for the hydroxyl hydrogen were calculated via Kraitchman's equations[14] and are listed in Table 5.[15] This provides the clearest identification of the observed species as **5**. For this species the substituted nucleus would lie in the *ac* plane. The small observed value of the substitution coordinate $|b|$ is consistent with this equilibrium structure.

Geometry. The energy ranking of the most extended (and presumably least sterically hindered) trans conformer as the next lowest in energy after the π-cloud H-bond stabilized species may be a general result for 2-substituted ethanols, since this relationship is observed also in the analogous case of 2-vinylethanol.[5] However, as Murcko and DiPaola pointed out,[1] there are cases (e.g., difluoroethane) where the gauche conformer is of lower energy than trans, indicating that factors other than hydrogen bonding can sometimes be involved in stabilizing the gauche conformer. The energy differences between the most extended conformer and some adjacent conformers are relatively small for both 2-phenylethanol and 2-vinylethanol.

Conformer Abundances. In jet expansion spectroscopy of molecules with multiple conformers, all of the conformers are brought into thermodynamic equilibrium at the preexpansion temperature, under pressure conditions where the collision rate is high (ca. 10^{10} s^{-1}). During the expansion, at a rate depending on the interconformational energy barriers and the composition of the drive gas (and plausibly upon the preexpansion temperature and the size and polarity of the substrate molecule) some conformer pairs will relax.[9,16] The postexpansion relative populations of such conformer pairs will reflect an equilibration temperature approaching the very low rotational temperature achieved in the jet expansion. Therefore, except in the very rare case that the two conformers differ in energy by less than ca. 10 K, the population of the lower energy conformer in the relaxing pair will, after expansion, contain the sum of the preexpansion populations of the relaxing pair. In cases where this lower member is also the upper conformer of another relaxing pair, the population will be funneled into the still lower conformer. In this way it is anticipated that the populations in the five distinct conformers of 2-phenylethanol prior to expansion from 573 K will be funneled into just two conformers (**1** and **5**) following the free-jet expansion in argon.

It is possible to predict the relative populations before and after expansion from the theoretical Gibbs energy of each conformer calculated with data from the ab initio calculations. The largest term in the relative energy differences is the Born−Oppenheimer energy (in our case approximated at the MP2 level). Significant contributions also arise from the vibrational zero-point energy. This usually is calculated under the assumption of harmonic vibrations, which may be a poor approximation, particularly for the lower frequency torsional modes of a flexible molecule. However, these contribute a relatively small amount to the total zero point energy, which is dominated by the stretching and bending modes. Prior to expansion the temperature-dependent vibrational contribution to the Gibbs energy is significant and is largely associated with occupancy of excited states in the low-frequency modes. The harmonic approximation is a more serious source of error in this case. In extreme cases of anharmonicity several conformers may coalesce, e.g., into a manifold of free rotor states, necessitating explicit treatment of anharmonicity in calculating the Gibbs energy.[17]

Following expansion, the vibrational temperature of the low-frequency modes is effectively zero, so that only the Born−Oppenheimer and zero-point energies will contribute to the Gibbs energy. However, equilibration (strictly speaking, quasi-equilibration) will occur only between those conformers separated by a sufficiently low energy barrier to permit interconformational relaxation during the expansion. Because of the extremely low temperature characterizing the equilibration of the relaxed conformers, the relative Gibbs energy in this case simply serves to indicate the lowest energy conformer in each relaxing set to which all the preexpansion population from the set will be funneled.

Both before and after expansion the influence of 2-fold enantiomeric degeneracy must be adequately accounted for in the populations of conformers lacking a plane of symmetry.

Table 3 shows for each conformer the relative Born−Oppenheimer energies calculated at the MP2/6-311++G(d,p) level, the zero-point corrected energies (where the harmonic frequencies were calculated at the MP2/6-31G(d,p) level and have been multiplied by a frequency scaling factor of 0.9910[4b]), and the relative Gibbs energies prior to expansion. The consequent theoretical relative populations before and after expansion also are shown. By use of an analogous calculation for the equilibrium relative abundances at ambient temperature (298 K), conformer **1** is predicted to have over 5 times the abundance of the next species (conformer **4**). However, it should be noted that this prediction applies to the vapor phase and that intermolecular interactions may influence significantly the abundances in the liquid and solid states.

The approximate observed relative abundances of conformers **1** and **5** have been estimated from the observed relative intensities in the microwave absorption spectrum. In making this estimation it is necessary to make some rather crude assumptions relating to the thermal state of the jet-cooled molecules. A uniform global rotational temperature is assumed, although it is by no means clear that the conformers have relaxed to a common rotational temperature (or indeed that all the rotational states in a given conformer are characterized by a single rotational temperature). From relative intensity measurements the population of conformer **1** appears to exceed **5** by a factor of ca. 2. This rather imprecise experimental value is not inconsistent with the theoretical prediction of 1.6 given in Table 3.

Conclusion

We have detected via microwave spectroscopy and rotationally assigned the spectrum of a second conformer of 2-phenylethanol. Through comparison of measured and ab initio MP2/6-311++G(d,p) predicted theoretical rotational constants, deuterium substitution coordinates, and dipole moment components we have shown that the new conformer is the extended trans form-**5**. This is in agreement with the conclusions of UV−IR laser expansion jet spectroscopy.[8] Our failure to identify any additional conformers, other than the previously reported **1**, in the jet-expanded microwave spectrum is consistent with the conformational relaxation processes anticipated from the ab initio interconformational energy barriers reported previously.[3]

This study supports the view that ab initio calculations at least as elaborate as the MP2/6-311++G(d,p) level may be necessary to provide relative energetic predictions for conformers that are adequately reliable for the interpretation of jet-cooled spectra of organic molecules.

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Supporting Information Available: Tables 1S−5S containing all the measured and assigned microwave transition frequencies used to derive the rotational constants reported in this work, all the measured and assigned Stark shifts used to derive the dipole moment components reported in this work, and the complete ab initio optimized geometries for each structural form of 2-phenylethanol. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Murcko, M. A.; DiPaoli, R. A. *J. Am. Chem. Soc*. **1992**, *114*, 10010−10018.

(2) Godfrey, P. D.; Hatherley, L. D.; Brown, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 8204.

(3) Godfrey, P. D.; Jorissen, R. N.; Brown, R. D. *J. Phys. Chem. A* **1999**, *103*, 7621−7626.

(4) (a) Vogelsanger, B.; Godfrey, P. D.; Brown, R. D. *J. Am. Chem. Soc*. **1991**, *113*, 7864. (b) Godfrey, P. D.; Brown, R. D. *J. Am. Chem. Soc*. **1998**, *120*, 10 724−10 732.

(5) Crofts, J. G.; Brown, R. D.; Godfrey, P. D. *J. Phys. Chem. A* **1999**, *103*, 3629−3635.

(6) Marstokk, K. M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1981**, *35*, 395−401.

(7) Dickinson, J. A.; Hockridge, M. R, Kroemer, R. T.; Robertson, E. G.; Simons, J. P.; McCombie, J.; Walker, M. *J. Am. Chem. Soc*. **1998**, *120*, 2622−2632.

(8) Mons, M.; Robertson, E. G.; Snoek, L. S.; Simons J. P. *Chem. Phys. Lett*. **1999**, *310*, 423−432.

(9) Godfrey, P. D.; Brown, R. D.; Rodgers, F. M. *J. Mol. Struct*. **1996**, *376*, 65−81.

(10) Brown, R. D.; Crofts, J G.; Godfrey, P. D.; McNaughton, D.; Pierlot, A. P. *J. Mol. Struct*. **1988**, *190*, 185−193.

(11) Patel, D.; Margolese, D.; Dyke, T. R. *J. Chem. Phys*. **1979**, *70*, 2740.

(12) Gaussian 94, Revision B.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Marcel Dekker: New York, 1977; pp 1−89.

(14) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.

(15) In Table 5 of ref 3 the data were inadvertently described as being derived from calculations at the MP2/6311++G(d,p) level but in fact are MP2/6-31G(d,p) data. It will be seen that the values differ slightly from those in the present Table 5, but the arguments based on them in ref 3 are unaffected.

(16) (a) Felder, P.; Günthard, H. H. *Chem. Phys*. **1982**, *71*, 9−25. (b) Ruoff, R. S.; Klots, T. D.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys*. **1990**, *93*, 3142−3150.

(17) Godfrey, P. D.; Mirabella, M.; Brown, R. D.; *J. Phys. Chem. A* **2000**, *104*, 258−264.