12290 *J. Am. Chem. Soc.* **2001,** *123,* 12290−12293

The Nature of Improper, Blue-Shifting Hydrogen Bonding Verified Experimentally

Benjamin J. van der Veken,[†] Wouter A. Herrebout,[†] Roman Szostak,[‡]
Dimitrij N. Shchepkin,[§] Zdenek Havlas,[∥,⊥] and Pavel Hobza*,[⊥,#]

Contribution from the Department of Chemistry, Universitair Centrum Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium, Department of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland, Institute of Physics, St. Petersburg University, Peterhof Campus, 198904 St. Petersburg, Russia, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague 6, Czech Republic, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic, and Center for Complex Molecular Systems and Biomolecules, 182 23 Prague 8, Czech Republic

Received April 9, 2001

Abstract: In the infrared spectra of solutions in liquid argon of dimethyl ether ($(CH_3)_2O$) and fluoroform (HCF_3), bands due to a 1:1 complex between these monomers have been observed. The C−H stretch of the HCF_3 moiety in the complex appears 17.7 cm^{-1} above that in the monomer, and its intensity decreases by a factor of 11(2). These characteristics situate the interaction between the monomers in the realm of improper, blue-shifting hydrogen bonding. The complexation shifts the C−F stretches downward by some 9 cm^{-1}, while the C−H stretches in $(CH_3)_2O$ are shifted upward by 9−15 cm^{-1}, and the C−O stretches are shifted downward by 5 cm^{-1}. These shifts are in very good agreement with those calculated by means of correlated ab initio methods, and this validates a two-step mechanism for improper, blue-shifting hydrogen bonding. In the first step, the electron density is transferred from the oxygen lone electron pairs of the proton acceptor ($(CH_3)_2O$) to fluorine lone electron pairs of the proton donor (CHF_3) which yields elongation of all CF bonds. Elongation of CF bonds is followed (in the second step) by structural reorganization of the CHF_3 moiety, which leads to the contraction of the CH bond. It is thus clearly demonstrated that not only the spectral manifestation of H-bonding and improper H-bonding but also their nature differ.

Introduction

The importance of hydrogen bonding, with its pervasive influence on the spatial structure of molecules of biological interest, can hardly be overemphasized. A hydrogen bond is formed when the hydrogen atom of a covalent A−H bond of a proton donor molecule interacts with a lone electron pair of an atom X of a proton acceptor. The formation of the H-bond weakens the A−H bond, causing elongation of the A−H bond and a concomitant lowering (red shift) of the A−H stretching frequency. These characteristics are regarded as an unambiguous signature of the H-bond.[1−3]

Indications that the situation might be different in some systems started to surface from 1989 onward. Experimental and theoretical studies showed that in some cases the A−H···X contact gives rise to an unexpected blue shift of the A−H stretch.[4−16] The shift may be up to 30 cm^{-1} in neutral and more than 100 cm^{-1} in ionic complexes.[11] This new type of H-bonding has become known as *improper*, *blue-shifting* H-bonding.[11]

The nature of the classical H-bond is well understood: it is generally accepted[1] that electron density (ED) is transferred from the proton acceptor to the antibonding σ^* orbital of the A−H bond, explaining both the elongation and the red shift. Despite intense experimental and theoretical investigation, there remains disagreement on the explanation of the blue-shifting phenomenon. Some authors[12−15] favor the view that there are no basic differences in the nature of red- and blue-shifting H-bonds. Having a different view, we have suggested a two-step mechanism that involves ED transfer (EDT) from the proton acceptor

---

[*] Corresponding author: (e-mail) hobza@indy.jh-inst.cas.cz.

[†] Universitair Centrum Antwerpen.

[‡] University of Wrocław.

[§] St. Petersburg University.

[∥] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic.

[⊥] Center for Complex Molecular Systems.

[#] J. Heyrovský Institute, Academy of Sciences of the Czech Republic.

(1) Scheiner, S. *Hydrogen Bonding. A Theoretical Perspective*; Oxford University Press: Oxford, U.K., 1997.

(2) Desiraju, G. R.; G. R.; Steiner, T. *The Weak Hydrogen Bond;* Oxford University Press: Oxford, U.K., 1999.

(3) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(4) Buděšinský, M.; Fiedler, P.; Arnold, Z. *Synthesis* **1989**, 858.

(5) Boldeskul, I. E.; Tsymbal, I. F.; Ryltsev, E. V.; Latajka, Z.; Barnes, A. J. *J. Mol. Struct.* **1977**, *436*, 167.

(6) Contréras, R. H.; Peralta, J. E.; Giribet, C. G.; Ruiz de Azua, M. C.; Faceli, J. C. Annu. Rep. NMR *Spectrosc*. **2000**, *41*, 55.

(7) Tokhadze, K. G. In *Molecular Cryospectroscopy*; Clark, R. J. H.; Hester, R. E., Eds.; Wiley: Chichester, U.K., 1995; p 160.

(8) Hobza, P.; Špirko, V.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem. A* **1998**, *102*, 250.

(9) Barth, H.-D.: et al. *Chem. Phys.* **1998**, *239*, 49.

(10) P. Hobza P.; Špirko, V.; Havlas, Z.; Buchhold, K.; Reimann, B.; Barth, H.-D.; Brutschy, B. *Chem. Phys. Lett.* **1999**, *299*, 180.

(11) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

(12) Gu, Y.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.

(13) Gu, Y.; Scheiner, S.; Kar, T. *J. Mol. Struct.* **2000**, *552*, 17.

(14) Scheiner, S.; Gu, Y.; Kar, T. *THEOCHEM* **2000**, *500*, 441.

(15) Scheiner, S. *Adv. Mol. Struct. Res.* **2000**, *6*, 159.

(16) Salvador, P.; Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **2000**, *113*, 5666.

10.1021/ja010915t CCC: $20.00

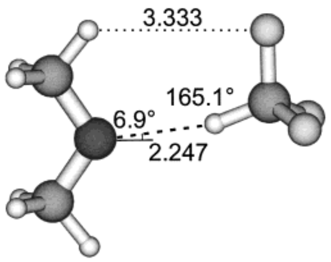

Figure 1. MP2/6-31G* CP-corrected geometry for $(CH_3)_2O{\cdot}HCF_3$.

to the remote part of the proton donor, causing it to structurally relax, which in turn leads to a shortening of the A−H bond.[11]

Essential to the proposed mechanism is that it not only influences the A−H bond but causes predictable shifts in the vibrations of the remote part of the H-donor as well. The main goals of the present paper, therefore, are to provide vibrational data in a sufficiently wide frequency window to allow detailed comparison with theoretical predictions and to show that the observations are in support of the two-step mechanism.

The complex under scrutiny is the one formed between dimethyl ether ($(CH_3)_2O$) and fluoroform (HCF_3). Quantitative data on the EDT have been obtained from ab initio calculations, while the formation of the complex has been studied with infrared spectroscopy in cryosolutions, using liquid argon as the solvent.[17]

Experiments

Experimental conditions used for recording the infrared spectra of cryosolutions were as described before.[17] Infrared spectra of a series of mixtures in liquid argon, containing mole fractions of $(CH_3)_2O$ ranging from 1.5×10^{-5} to 6×10^{-4} and containing HCF_3 with mole fractions from 0.5×10^{-5} to 7×10^{-4}, were investigated.

Calculations

Ab initio structures of a complex and subsystems were determined using standard and counterpoise-corrected (CP) gradient optimization[18] at the MP2/6-31G* level. Traditional and CP-corrected harmonic frequencies were evaluated for all structures; no scaling was applied. Natural bond orbital (NBO) analysis[19] was performed using the MP2 electron density. The stabilization energy of the complex was determined at the MP2/aug-cc-pVXZ (X = D, T) level and at CCSD(T) level using 6-31G** and 6-31++G** basis sets; the basis set superposition error was systematically removed by applying the standard function counterpoise method proposed by Boys and Bernardi.[20] All calculations were performed using GAUSSIAN98.[21]

Results and Discussion

Correlated ab Initio Calculations. The structure of $(CH_3)_2O{\cdot}HCF_3$ is shown in Figure 1; its characteristics are collected in Tables 1 and 2. Following expectation, the MP2 and CCSD(T) stabilization energies differ only slightly. The genuine stabilization energy is estimated from the aug-cc-pVTZ MP2 stabilization energy and a [MP2 − CCSD(T)] stabilization energy difference evaluated at the 6-31++G** level. The estimated stabilization energy is ~3.9 kcal mol^{-1}. Because enlarging of the AO basis set yields a slight increase of stabilization energy, the estimated value represents the lower limit of the genuine stabilization energy. Taking the MP2/6-31G* zero-point energies into account, the lower limit of the stabilization enthalpy can be estimated at 3.3 kcal mol^{-1}.

Table 1. Complexation Energies (in kcal mol^{-1}) for $(CH_3)_2O{\cdots}HCF_3$

method	6-31G*[a]	6-31G*[b]	6-31++G**	aug-cc-pVDZ[c]	aug-cc-pVTZ[c]
MP2	3.24	3.30	3.91	3.67	3.93
CCSD(T)	3.20		3.88		

[a] Obtained using standard optimization procedures. [b] Obtained using CP-corrected gradients. [c] Single-point energies obtained using the MP2/6-31G* CP-corrected geometry.

For HCF_3, formation of the complex leads to contraction of the C−H bond and elongation of all C−F bonds, with concomitant blue shift of the C−H stretch (31 cm^{-1}) and red shifts of the C−F stretches (9, 10, and 11 cm^{-1}). Previous calculations[11] have shown that inclusion of anharmonicity reduces the blue shift of C−H stretches by ~10 cm^{-1}. Thus, a realistic estimate of the experimental blue shift of the C−H stretch frequency is ~20 cm^{-1}. While the infrared intensity of the C−H stretch decreases substantially upon complexation, intensities of the C−F stretches are hardly changed. All these features differ from the characteristics of the classical H-bonds.

The NBO analysis of monomers and complex reveals an EDT from $(CH_3)_2O$ to HCF_3. The EDT originates from the oxygen lone pairs and is mainly directed to the lone pairs of fluorine atoms and, to a lesser extent, to the σ^* antibonding orbital of the HCF_3 C−H bond. The increased electron density at the fluorine atoms leads to elongation of the C−F bonds,[22] while an increase of electron density in the C−H σ^* antibonding orbital weakens the C−H bond, which should be accompanied by its elongation. The elongation of the C−F bonds, however, is followed by the structural reorganization of the HCF_3 subsystem, which, instead, leads to the contraction of the C−H bond.[23] Evidently, the contraction dominates over the elongation, and the net overall effect is a shortening of the C−H bond upon complexation (see Table 2).

From Table 2, it is evident that elongation of CF bonds is in absolute value larger than the contraction of the CH bond. This is an important feature distinguishing H-bonding and improper, blue-shifting H-bonding. The dominant geometry change occurred in the former complexes at the X−H bond of the proton donor while in the latter complexes it occurred at a remote (nonparticipating) part of the proton donor. For strong and medium H-bonded complexes, this difference is clearly pronounced. In the case of water dimer, the OH bond length increased upon formation of an H-bond by 0.0066 Å while the other (nonparticipating) OH bond contracted by 0.0009 Å (MP2/cc-pvTZ). For weaker H-bonds, the situation is analogous and supporting arguments can be found in a recently published paper by Hartmann et al.[24] The authors investigated the acetylene-containing complexes with C−H⋯Y contacts and found that

---

(17) Herrebout, W. A.; Szostak, R.; Van der Veken, B. J. *J. Phys. Chem. A* **2000**, *104*, 8480.

(18) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024.

(19) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(20) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(21) Frisch, M. J.; et al. *GAUSSIAN98* (Rev. A1); Gaussian, Inc.: Pittsburgh PA, 1998.

(22) Elongation of the C−F bonds by increased negative charge at fluorine atoms was modeled by adding a He atom 1.5 Å next to the hydrogen atom, at the HF/6-31G* level. The helium atom transfers charge of 0.004 electron to each fluorine atom. Keeping all geometrical parameters fixed, except the C−F bonds, leads to a CF bond elongation of 0.0023 Å.

(23) The fact that the contraction of the C−H bond in the CHF_3 subsystem is due to elongation of C−F bonds can be easily proven by gradient optimization of the CHF_3 system in which artificially elongated C−F bonds are kept constant during the optimization: Elongation of CF by 0.005 (0.01) Å stretches CH bond length by 0.0006 (0.0010) Å. Opening of the H−C−F angle by 1° stretches the CH bond by 0.0007 Å and the CF bond by 0.0014 Å.

(24) Hartmann, M.; Wetmore, S. D.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 4470.

Table 2. Physical Properties of $(CH_3)_2O{\cdot}HCF_3$[a]

Δr(CH)/Å	Δr(CF)/Å	$\Delta\nu$(CH)/cm^{-1}	ΔI[b]	$\Delta\nu$(CF)/cm^{-1}	ΔI[b]	EDT/e[c]	ΔED(CF)/e[d]	ΔED(CH)/e[e]
−0.0015	0.0048	31	47 → 1	−11	244 → 244	0.0101	0.0018	0.0023
	0.0034			−10	244 → 218		0.0015	
	0.0034			−9	107 → 148		0.0015	

[a] All values refer to the MP2/6-31G* CP-corrected geometry. [b] Variation of the infrared intensity upon complexation. All intensities are given in km mol^{-1}. The absolute values for the CH and the CF_3 stretches in the complex are 3266, 1161, 1205, and 1206 cm^{-1}. [c] Electron density transfer. [d] Increase of electron density at the fluorine lone pairs. [e] Increase of electron density in the CH δ antibonding orbital.

Table 3. Characteristic Vibrational Frequencies (in cm^{-1}) for $(CH_3)_2O{\cdots}HCF_3$

	monomer	complex
$\nu_6^{CH_3OCH_3}$	930.4	924.0
$\nu_{17}^{CH_3OCH_3}$	1100.2	1097.4
$\nu_{16}^{CH_3OCH_3}$	1173.7	1169.1
$\nu_1^{HCF_3}$	3036.7	3054.4
$\nu_2^{HCF_3}$	1134.5	1122.4
$\nu_5^{HCF_3}$	1144.7	1132.6

C−H bonds were lengthened by up to 0.009 Å while the CC triple bond was lengthened only up to 0.002 Å. To stress this point further, we studied the $(CH_3)_2O{\cdots}HCN$ complex (MP2/aug-cc-pVDZ). Calculated characteristics supported the existence of H-bond: the C−H bond was elongated by 0.0102 Å while the CN triple bond was elongated only by 0.0003 Å. For the sake of comparison, let us mention here also the geometrical changes of the $(CH_3)_2O{\cdots}HCF_3$ complex obtained at the same theoretical level: the CF bonds were elongated by 0.0048, 0.0034, and 0.0034 Å while the CH bond was contracted by 0.0015 Å. The different position of a dominant geometry change in both types of H-bonded complexes is also reflected by a different value of H-index for these two types of H-bonded complexes.[25] The recently introduced H-index (the ratio of the increase of electron density in the X−H antibonding σ^* orbital to the total EDT between proton acceptor and proton donor) lies in the interval 0.7−1.0 for H-bonded complexes while it is close to 0 for improper H-bonded complexes. This reflects a different target of EDT in both complexes: X−H bond in the proton donor in the H-bonded complexes and remote (non-participating) part of the proton donor in the improper H-bonded complexes.

The NBO analysis also reveals changes in the ED of $(CH_3)_2O$. The electron density reduction in the oxygen lone pairs (0.002 e) is accompanied by a slight electron density enhancement in the σ^* antibonding orbitals of the C−O bonds and by a small reduction in σ^* antibonding orbitals of all C−H bonds. The elongation of the C−O bonds, by 0.004 and 0.003 Å, and the shortening of most of the C−H bonds, by 0.001 Å, is reflected in the red shifts of some 5 cm^1 for the C−O stretches and in blue shifts, varying between 9 and 15 cm^{-1}, for the C−H stretches.

IR Spectroscopy in Cryosolutions. In a previous infrared study of this complex,[7] we detected the blue shift of the A−H stretch frequency but did not observe the changes in the other vibrations, preventing unambiguous support for the two-step mechanism to be obtained. The same is true for our previous infrared studies[11] where we detected only the shifts in the C−H stretches. The solutions of $(CH_3)_2O$ and HCF_3 in liquid argon have been reinvestigated, and we have identified the modes of the complex essential for the present purposes. Determination of the stoichiometry of the complex as described previously[17] confirms that the 1:1 complex was formed. Wavenumbers of relevant complex bands and their assignment are given in Table 3. In Figure 2, the 3100−2750-cm^{-1} region of the spectrum of a solution containing both $(CH_3)_2O$ and HCF_3 (a) is compared with that of a solution containing only $(CH_3)_2O$ (b) or HCF_3 (c). Comparison of the difference spectrum d, obtained by subtracting properly rescaled spectra b and c from a, shows that in the complex a new, weak band, which we assign as the C−H stretch of the HCF_3 moiety of the complex, is observed at 3054.4 cm^{-1}, blue hifted by 17.7 cm^{-1} from the corresponding monomer frequency. This result agrees well with the estimated anharmonic shift of ~20 cm^{-1}. Analysis of the temperature behavior of the 3010−3070-cm^{-1} region leads to a monomer-to-complex intensity ratio for the C−H stretch mode of 11(2), in qualitative agreement with the theoretical predictions.

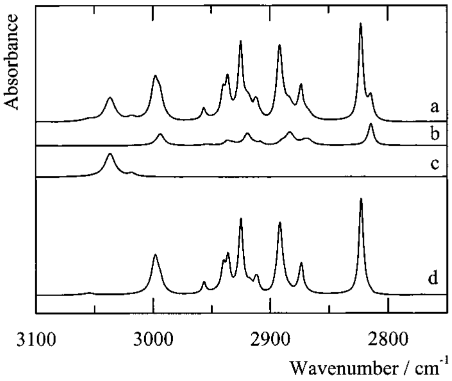

Figure 2. Infrared spectra of solutions in liquid argon in the CH stretching region, recorded at 92 K: (a) mixture of $(CH_3)_2O$ and HCF_3; (b) solution containing only $(CH_3)_2O$; (c) solution containing only HCF_3; (d) difference spectrum resulting from the subtraction of properly rescaled traces b and c from a. The mole fractions for $(CH_3)_2O$ and HCF_3 used in (a) are 2.5×10^{-4} and 3.0×10^{-4}.

The region of the CF_3 antisymmetric and symmetric stretches is shown in Figure 3A. For monomer HCF_3, Figure 3c, the stretches are detected at 1144.7 and 1134.5 cm^{-1}, assigned as the antisymmetric (ν_5) and the symmetric CF_3 stretches (ν_2), respectively.[26] In the spectrum of the mixed solution, Figure 3a, new bands become prominently visible at 1134.6 and 1124.2 cm^{-1}, i.e., red shifted by 10.1 and 10.3 cm^{-1}. We assign these bands as the CF_3 antisymmetric and symmetric stretches of the complex. The assignments are confirmed by the observation of complex bands in the vicinity of $2\nu_2$, $2\nu_5$, $\nu_2 + \nu_5$, $\nu_5 + \nu_6$, $\nu_2 + \nu_3$, and $\nu_2 + \nu_5$ of monomer HCF_3. The experimental findings agree very well with the theoretical predictions of red shifts of 9, 11, and 11 cm^{-1}, respectively.

The spectra further allow identification of complex bands for modes localized in $(CH_3)_2O$. In the C−H stretch region, Figure 2, the complex bands are found blue shifted by 9−15 cm^{-1} from their monomer counterparts. This agrees with results obtained for a variety of complexes observed in solid matrixes.[27−29] The small blue shifts can be explained[29] by a partial reduction by the Lewis acid of the lone pair effect.[30]

---

(25) Hobza, P. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2555.

(26) Amrein, A.; Quack, M.; Schmitt, U. *Mol. Phys.* **1987**, *60*, 237.

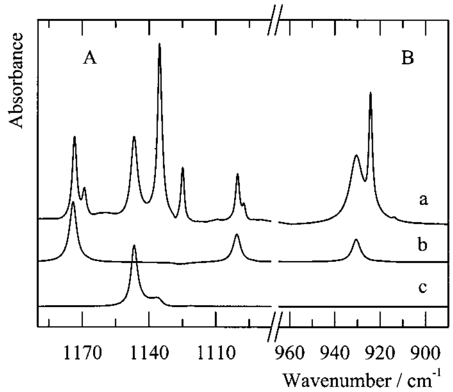

Figure 3. The 1175−1105-^{1} (A) and 960−900-cm^{-1} (B) spectral regions of solutions in liquid argon containing (a) both $(CH_3)_2O$ and HCF_3, (b) only $(CH_3)_2O$, and (c) only HCF_3. The mole fractions for $(CH_3)_2O$ and HCF_3 used in (A) are 4.5×10^{-4} and 0.5×10^{-5} and those used in (B) are 3.0×10^{-4} and 3.5×10^{-4}. All spectra were recorded at 92 K.

This is in full accord with our NBO analysis, and the measured blue shifts agree with the calculated values.

In Figure 3A, complex bands are also observed for the CH_3 rocking mode and the C−O−C antisymmetric stretch, which in monomer $(CH_3)_2O$ are situated near 1173.7 and 1100.2 cm^{-1}. A similar pattern is observed for the C−O−C symmetric stretch, the region of which is shown in Figure 3B. The observed frequency shifts of the O−C−O modes, −2.8 and −6.4 cm^{-1}, again compare well with the calculated values.

The complexation enthalpy $\Delta H°$ for $(CH_3)_2O\cdots HCF_3$ was derived from a Van't Hoff analysis, corrected for thermal expansion of the solution.[31,32] Spectra of a mixed solution were recorded at 12 different temperatures between 86 and 119 K. Using different sets of vibrational bands of monomers and complex, an average $\Delta H°$ of −3.04(7) kcal mol^{-1} was obtained. This value agrees well with the above gas-phase estimate (including zero-point energy) of −3.3 kcal mol^{-1}.

Conclusion

By employing infrared spectroscopy in cryosolutions, important fundamentals in the infrared spectrum of the complex $(CH_3)_2O\cdots HCF_3$ have been identified. The C−H stretch of the HCF_3 moiety in the complex is blue shifted by 17.7 cm^{-1}, so that the interaction between the monomers is an improper, blue-shifting hydrogen bond. All observed frequency shifts agree very well with predictions from correlated ab initio calculations. The NBO analysis of the latter shows that the bonding in the complex follows the two-step mechanism recently proposed for this type of hydrogen bonding. Thus, the agreement of experiment with prediction validates the two-step mechanism. It is, therefore, concluded that improper, blue-shifting hydrogen bonding differs from its classical counterpart.

Acknowledgment. W.A.H. thanks the FWO-Vlaanderen for an appointment as Postdoctoral Fellow. Gratitude is expressed to the FWO for their assistance toward the purchase of spectroscopic equipment used in this study. The authors thank the Flemish Community for financial support through Bilateral Cooperation between Flanders and Poland, and through the Special Research Fund (BOF). Financial support by the Center for Complex Molecular Systems and Biomolecules, Czech Republic (Project LN00A032 of MSMT CR) is acknowledged.

JA010915T

---

(27) Han, S. W. Kim, K. *J. Mol. Struct.* **1999**, *475*, 43.

(28) Goebel, J.; Ault, B. S.; Del Bene, J. E. *J. Phys. Chem. A* **2000**, *104*, 2033.

(29) Andrews, L.; Johnson, G. L.; Davis, S. R. *J. Phys. Chem.* **1985**, *89*, 1710.

(30) Bellamy, L. J.; Mayo, D. W. *J. Phys. Chem.* **1976**, *80*, 1217.

(31) Bertsev, V. V.; Golubev, N. S.; Shchepkin, D. N. *Opt. Spektrosk.* **1976**, *40*, 951.

(32) Van der Veken, B. J. *J. Phys. Chem.* **1996**, *100*, 17436.