

## Vibrational Zeeman Effect for the $\nu_4$ Mode of Haloforms ( $\text{HCX}_3$ ) Determined by Magnetic Vibrational Circular Dichroism

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The magnetic vibrational circular dichroism (MVCD) spectra of the  $E$ -symmetry,  $\nu_4$  modes of  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ ,  $\text{HClI}_3$ , and  $\text{DCCl}_3$  are presented. In each case, an MVCD  $A$  term indicating a first order vibrational Zeeman effect is observed. The vibrational  $g$  values for the  $\nu_4$  mode of these haloforms were determined for the first time by moment analysis of the MVCD and absorption spectra. A partially charged "elastic bar" model is proposed to qualitatively explain the observed MVCD  $A$  terms.

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The rotational Zeeman effect has been studied for many years, mainly by microwave spectroscopy and molecular beam magnetic resonance methods. Almost all of those studies have been focused on the Zeeman effect in the ground vibrational state of relatively small molecules because of the difficulty of measuring the Zeeman effect in excited vibrational states using conventional techniques. The analogous vibrational Zeeman effect has been theoretically described by Howard and Moss [1] as one component in the Hamiltonian for a general rotating, vibrating molecule. There have been few experimental measurements of the vibrational Zeeman effect, with those by Hüttner and co-workers using microwave techniques being notable exceptions [2-4].

We have developed a new molecular Zeeman technique, magnetic vibrational circular dichroism (MVCD) [5,6], the differential absorption of left and right circularly polarized light by a sample in a magnetic field collinear with the light propagation direction. MVCD can measure the molecular Zeeman effect  $g$  values for various vibrationally excited states which are accessible in the infrared [7-9]. Because it is an intensity measurement, MVCD can never have the quantitative accuracy of conventional high resolution techniques based on frequency measurement of the Zeeman shifts. However, MVCD intensities are highly sensitive to small Zeeman splittings, permitting measurement of "high resolution phenomena" with a low resolution spectrometer. For example, Zeeman splittings 3 orders of magnitude smaller than the spectrometer resolution can be easily measured with reasonable accuracy using MVCD. As a consequence, MVCD is useful even for condensed phase molecules [5,10-12].

Here we report the first MVCD results for the  $\nu_4$  vibrational mode of the haloforms ( $\text{HCX}_3$ ,  $X = \text{Cl, Br, I}$ ) in both the gas and liquid solution phases. Analyses of these data lead to the first determination of the vibrational Zeeman effect for this mode in those species.

The MVCD spectra were measured using a Digilab FTS-60 based Fourier transform infrared (FTIR) VCD spectrometer combined with an Oxford superconducting

magnet which has been described in detail elsewhere [6,12,13]. The optical and electronics design are the same as previously used for our rotationally resolved MVCD studies [7,8].

$\text{HCCl}_3$ ,  $\text{HCBBr}_3$ ,  $\text{HClI}_3$ , and  $\text{DCCl}_3$  and the  $\text{CS}_2$  solvent were obtained commercially (Aldrich) and used without further purification. The MVCD of  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{HClI}_3$  in  $\text{CS}_2$  solution were measured using a cell composed of two KBr windows and a 2 mm Teflon spacer. Gas phase spectra for  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{DCCl}_3$  were measured by expanding them into a 5 cm path length brass cell sealed with KBr windows to obtain an absorbance maximum between 0.3 and 1.0 at the  $4 \text{ cm}^{-1}$  resolution used.

The MVCD and absorption spectra for the  $\nu_4$  mode of  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{HClI}_3$  in  $\text{CS}_2$  solution are shown in Fig. 1. In each case, MVCD was observed having a derivative shape with its negative component to high energy, which is termed a negative  $A$  term [14]. Relatively strong signals (in terms of  $\Delta A/A$ ) with little change between the halogens were seen (Table I). To compare the Zeeman characteristics of the haloforms in solution to those in the gas phase, we also measured the MVCD of

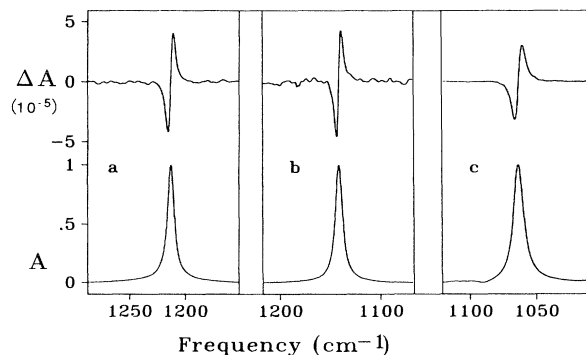


FIG. 1. MVCD and absorption spectra of  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{HClI}_3$  measured in  $\text{CS}_2$  solution. MVCD spectra are normalized to 1 T. Absorption spectra are normalized to  $A_{\text{max}} = 1.0$ .

TABLE I. Moment analysis results for haloforms.

Haloforms	$\nu_0$ ( $\text{cm}^{-1}$ )	$\langle A \rangle_0$ ( $10^{-3}$ )	$\langle \Delta A \rangle_1$ ( $10^{-7}$ )	$A_1/D_0$ ( $10^{-4}$ )	$g^{v=1}$ ( $\mu_N$ )
$\text{HCCl}_3(\text{CS}_2)$	1213.3	8.61	-14.3	-3.56	+0.33
$\text{HCBBr}_3(\text{CS}_2)$	1141.2	2.74	-5.42	-4.09	+0.38
$\text{HCl}_3(\text{CS}_2)$	1063.1	6.00	-10.2	-3.65	+0.34
$\text{HCCl}_3(\text{gas})$	1219.8	9.89	-22.0	-4.76	+0.44
$\text{HCBBr}_3(\text{gas})$	1148.1	2.53	-5.15	-4.36	+0.40
$\text{DCCl}_3(\text{gas})$	913.4	16.6	-16.8	-2.17	+0.20

vapor phase  $\text{HCCl}_3$  and  $\text{HCBBr}_3$ . Other than a small increase in intensity, the gas phase results were virtually the same as for the condensed phase (Fig. 2). Finally, to evaluate the isotope effect, we measured the MVCD of gas phase  $\text{DCCl}_3$  which had an  $A$  term of about half the intensity of  $\text{HCCl}_3$  at the appropriately shifted frequency [Fig. 2(c)].

The moment analysis method [14] was used to extract  $A_1$ , the MVCD  $A$ -term parameter, which is proportional to the difference in ground and excited vibrational state magnetic moments [14], and  $D_0$ , the transition dipole strength, from the first moment of the MVCD ( $\langle \Delta A \rangle_1$ ) and the zeroth moment of the absorption ( $\langle A \rangle_0$ ) spectra, respectively. To minimize the effects of noise and baseline shift on the determination of  $A_1$  and  $D_0$ , we curve fit the MVCD and absorption spectra and used these for the parameter determination. The moment analysis results for the solution and gas phase haloform spectra, including  $\nu_0$ ,  $\langle A \rangle_0$ ,  $\langle \Delta A \rangle_1$ , and  $A_1/D_0$  are listed in Table I. For the gas phase  $\text{HCCl}_3$  MVCD spectrum, a very good signal-to-noise ratio ( $S/N$ ) and a baseline with practically no offset was obtained. Consequently, the moments determined from the fit curve and by direct integration of the experimental spectrum are virtually identical. A negative

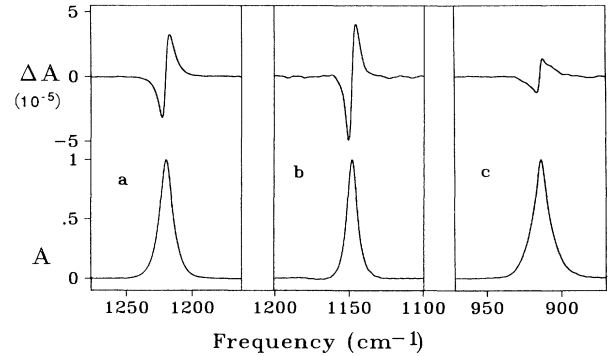


FIG. 2. MVCD and absorption spectra for  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{DCCl}_3$  measured in gas phase. Pressures: 32, 10, and 16 Torr for  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{DCCl}_3$ , respectively. MVCD spectra are normalized to 1 T. Absorption spectra are normalized to  $A_{\text{max}} = 1.0$ .

$A$ -term MVCD was also obtained for the  $\nu_4$  mode of  $\text{HCF}_3$ ; experiments studying its other vibrations and an alternate theoretical treatment are underway [12].

For the  $A \rightarrow E$  vibrational transition, by considering only the first order Zeeman effect, we can use an effective perturbation Hamiltonian of the form

$$H' = -\boldsymbol{\mu} \cdot \mathbf{B} = -g^{(v=1)} \mu_N B M_v, \quad (1)$$

where  $B$  is the magnetic field strength,  $\mu_N$  is the nuclear magneton, and  $M_v$  is the quantum number for the projection of vibrational angular momentum operator along the magnetic field. This perturbation can operate in the basis of  $|v, M_v\rangle$  states where  $v$ , the vibrational quantum number, can be 0 or 1, and  $M_v$  can be 0 or  $\pm 1$  for the ground and excited states, respectively. Modified expressions [14] for  $A_1$  and  $D_0$ , appropriate for MVCD, can be derived as follows:

$$A_1 = \sum_M \langle 1, \pm 1 | \mu_z | 1, \pm 1 \rangle (|\langle 0, 0 | m_- | 1, \pm 1 \rangle|^2 - |\langle 0, 0 | m_+ | 1, \pm 1 \rangle|^2) \\ = -g^{v=1} (\mu_N / \mu_B) B (|\langle 0, 0 | m_- | 1, +1 \rangle|^2 + |\langle 0, 0 | m_+ | 1, -1 \rangle|^2), \quad (2)$$

$$D_0 = \frac{1}{2} (|\langle 0, 0 | m_- | 1, +1 \rangle|^2 + |\langle 0, 0 | m_+ | 1, -1 \rangle|^2). \quad (3)$$

In these equations,  $\mu_z$  is the vibrational magnetic moment in the applied magnetic field direction,  $m_{\pm} = (m_x \pm im_y) / \sqrt{2}$  is the electric dipole moment operator for right and left circularly polarized light, respectively, and  $\mu_B$  is the Bohr magneton. These can be combined to give

$$g^{(v=1)} = -\frac{1}{2B} \frac{\mu_B}{\mu_N} \frac{A_1}{D_0}. \quad (4)$$

Using Eq. (4) and the moment analysis results, the vibrational Zeeman  $g$  values listed in the last column of Table I can be obtained. The negative  $A_1/D_0$  values determined for the  $\nu_4$  mode in all six spectra yield positive values of  $g^{v=1}$  as is clear from an analysis of the polarization of transitions to the Zeeman split  $|v, M_v\rangle$  states

[7–9]. These  $g$  values can then be compared to theoretical predictions for the vibrational Zeeman effect.

The vibrational Zeeman effect of the  $\nu_4$  mode for these haloforms can be modeled classically by the so-called “elastic bar” [15] with modification to include oscillation of a partial charge on the end of the “bar.” Since the carbon and halogen atoms are much heavier than the hydrogen atom, the  $\nu_4$ ,  $X$ -C-H deformation mode consists mainly of hydrogen atom motion. As we have confirmed by self-consistent field calculation for  $\text{HCF}_3$ , a partial positive charge is expected on the hydrogen atom due to the large electron affinity of the halogens [16].

For vibrational excitations with right and left circularly

polarized light, the phase difference between the  $x$  and  $y$  components of the  $\nu_4$ ,  $E$ -symmetry vibration can be taken as  $\pm \pi/2$ , corresponding to opposing senses of precession of the C-H bond around the molecular  $C_3$  axis. The resultant circular motion of the partially charged hydrogen atom leads to the vibrational magnetic dipole moment. When there is no magnetic field, the two vibrational components are degenerate, but in a magnetic field they will be split in frequency leading to  $A$ -term MVCD.

Using this model, a magnetic dipole moment of  $0.8\mu_N$  can be estimated for the  $\nu_4$  mode of  $\text{HCF}_3$  using a partial charge of 0.20 on the H atom [16], a vibrational frequency of  $1380\text{ cm}^{-1}$ , and an angle of deviation from the  $C_3$  axis of  $17^\circ$  (as estimated for a harmonic oscillator with a force constant of  $0.82\text{ m dyn \AA}$  [17]). Our experimental MVCD results for the  $\nu_4$  mode of  $\text{HCX}_3$  ( $X=\text{Cl, Br, or I}$ ) suggest that the  $v=1$  vibrational state has a magnetic dipole moment of  $(0.3\text{--}0.5)\mu_N$ . Considering the simplicity of this classical model, the agreement obtained with our experimental results is excellent.

We observed a smaller  $g$  value (0.20) for  $\text{DCCl}_3$  than for the  $\text{HCCl}_3$  which is also qualitatively consistent with the prediction of this model. Since deuterium substitution reduces both the vibrational amplitude and frequency for the  $\nu_4$  mode, but does not change the charge, a smaller magnetic moment would be expected.

From Table I it can be seen that somewhat higher  $g$  values were obtained for  $\text{HCCl}_3$  and  $\text{HCBBr}_3$  (less so) in the gas phase than in  $\text{CS}_2$  solution. In this classical model, such a change may arise from increased amplitude of H-atom motion in the gas phase. Alternatively, the Coriolis interaction [18] may cause the increased gas phase vibrational Zeeman effect. This perturbation enhances the elliptical motion of the hydrogen atom around the molecular axis and is normally considered to be the major contributor to the vibrational Zeeman effect of small gas phase molecules [18]. In some cases, the molecular vibrational Zeeman effect due to Coriolis coupling is substantial, as we have shown for the  $\nu_4$  mode of methane [8]. In the haloforms, since the rotational  $g$  value is small [19], the Coriolis contribution is expected to be small [18]. By contrast, the MVCD observed for the haloforms in  $\text{CS}_2$  solution should be due to molecular vibration alone since the molecular rotations of haloforms are presumably quenched in the solution phase. The similarity of the gas phase and solution phase results emphasizes the dominance of the vibrational Zeeman effect in these molecules. This is distinct from the examples of rotationally resolved MVCD we have previously reported [7,9] where the rotational Zeeman effect was the dominant effect.

The MVCD of the  $A_1$ -symmetry,  $\nu_1$  mode for  $\text{HCBBr}_3$  and  $\text{HCl}_3$  solution was previously reported [20] to consist of only MVCD  $B$  terms, which are single-signed MVCD bands due to the second order Zeeman effect mixing and shifting states [14]. In terms of  $\Delta A/A$ , for the same

magnetic field strength, those  $B$  terms were more than an order of magnitude weaker than the  $A$  terms shown in the figures here. It is expected that MVCD  $A$  terms would not be observed for the  $\nu_1$  mode since it is nondegenerate and the molecular rotations are quenched in the solution phase.

Previous MVCD studies of the haloforms [20] have been qualitatively interpreted in terms of a vibronic coupling model [21]. The increase in intensity with increasing haloform masses for the  $\nu_1$  mode MVCD correlated to the decrease in the respective electronic excited state energies. However, such a correlation is not seen for the  $\nu_4$  mode MVCD, indicating that the MVCD reported here is dominated by the nuclear contribution. Furthermore, predictions using the vibronic coupling model based on electronic MCD data for  $\text{HCl}_3$  [22] give an estimate of  $A_1/D_0$  that is an order of magnitude too small [12]. This further confirms the empirical observation above that the nuclear contribution dominates the observed  $\nu_4$  mode  $A$  terms and supports the appropriateness of the simple classical analyses above.

In conclusion, the MVCD  $A$  terms observed for the  $E$ -symmetry,  $\nu_4$  mode of several haloforms indicate that the spectra are dominated by the first order vibrational Zeeman effect. The vibrational  $g$  value for the  $\nu_4$  vibration is here obtained for the first time using the MVCD technique. The observed vibrational Zeeman effect can be approximately explained by the classical oscillation of the hydrogen atom modeled as a partially charged elastic bar.

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- [1] B. J. Howard and R. E. Moss, *Mol. Phys.* **19**, 433 (1970).
- [2] W. Hüttner and K. Z. Morgenstern, *Z. Naturforsch.* **25a**, 547 (1970).
- [3] W. Hüttner, H. K. Bodenseh, and P. Nowicki, *Mol. Phys.* **35**, 729 (1978); W. Hüttner, U. E. Frank, W. Majer, K. Mayer, and V. Špirko, *Mol. Phys.* **64**, 1233 (1988).
- [4] E. E. Uzgiris, J. L. Hall, and R. L. Barger, *Phys. Rev. Lett.* **26**, 289 (1971).
- [5] T. A. Keiderling, *J. Chem. Phys.* **75**, 3639 (1981).
- [6] T. A. Keiderling in, *Practical Fourier Transform Infrared Spectroscopy*, edited by J. R. Ferraro and K. Krishnan (Academic, San Diego, 1990), p. 203.
- [7] B. Wang, R. K. Yoo, P. V. Crotto, and T. A. Keiderling, *J. Phys. Chem.* **96**, 2422 (1992).
- [8] B. Wang, R. K. Yoo, P. V. Crotto, and T. A. Keiderling, *Chem. Phys. Lett.* **180**, 339 (1991); B. Wang and T. A. Keiderling (to be published).
- [9] C. N. Tam and T. A. Keiderling, *J. Mol. Spectrosc.* **157**, 391 (1993); B. Wang and T. A. Keiderling, *J. Chem. Phys.* **98**, 903 (1993).
- [10] T. R. Devine and T. A. Keiderling, *J. Chem. Phys.* **79**,

- 5796 (1983); **83**, 3749 (1985).
- [11] T. R. Devine and T. A. Keiderling, *J. Phys. Chem.* **88**, 390 (1984); P. V. Croatto and T. A. Keiderling, *Chem. Phys. Lett.* **144**, 455 (1988).
- [12] P. V. Croatto, Ph.D. thesis, University of Illinois at Chicago, 1990; B. Wang, Ph.D. thesis, University of Illinois at Chicago, 1993.
- [13] P. Malon and T. A. Keiderling, *Appl. Spectrosc.* **42**, 32 (1988).
- [14] P. J. Stephens, *Adv. Chem. Phys.* **35**, 197 (1976); S. B. Piepho and P. N. Schatz, *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism* (Wiley-Interscience, New York, 1983).
- [15] G. Herzberg, *Molecular Spectra and Molecular Structure II* (Van Nostrand, Princeton, NJ, 1945).
- [16] This partial charge was obtained by a self-consistent field calculation using a 6-31G basis set with the additional polarization functions of three Slater type *p* orbitals for H and three Slater type *d* orbitals for both C and F atoms.
- [17] A. Ruoff, H. Burger, and S. Biedermann, *Spectrochim. Acta* **27A**, 1359 (1971); **27A**, 1377 (1971).
- [18] R. E. Moss and A. J. Perry, *Mol. Phys.* **25**, 1121 (1973).
- [19] A. W. Ellenbreck and A. Dymanus, *Chem. Phys.* **35**, 227 (1978).
- [20] T. R. Devine and T. A. Keiderling, *Chem. Phys. Lett.* **124**, 341 (1986).
- [21] M. Pawlikowski and T. A. Keiderling, *J. Chem. Phys.* **81**, 4765 (1984).
- [22] A. Gedanken and M. D. Rowe, *Chem. Phys.* **36**, 181 (1979).