Vibrational Magnetic Dipole Moment of Acetylene in the ν_5 Mode

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Received: August 30, 1995; In Final Form: November 3, 1995[⊗]

The sign and approximate magnitude of the gyromagnetic ratio for the ν_5 doubly degenerate bending mode of acetylene are determined by use of rotationally resolved magnetic dichroism measurement of transitions to the singly excited vibrational state. By analysis of the *J*-dependence of the apparent *g*-value for this transition, the vibrational *g*-factor was determined from the experimental spectrum by moment analysis to be $g_v = 0.48(25)$. This is the first such determination of g_v in a degenerate state of a linear molecule using MVCD and the first determination of g_v for the ν_5 mode in acetylene. Simulated MVCD spectra based on the accepted ground state rotational *g*-value and this determination of g_v agree with the observed intensity pattern, confirming the analysis.

Introduction

Magnetic properties of diamagnetic molecules are of fundamental importance and provide theoretical and experimental challenges. Experimentally, the molecular Zeeman effect measured using microwave spectroscopy enables straightforward measurement of the rotational magnetic moment of small molecules in the ground state. As we have shown earlier, rotationally resolved magnetic vibrational circular dichroism (RR MVCD) can be used in many cases for a simple, convenient determination of the molecular magnetic moment in various excited vibrational states.[1]

Having access to excited vibrational states gives MVCD the potential to measure the magnetic moments that arise from vibrational motion in degenerate modes. We have reported observation of such an effect using MVCD for the ν_2 deformation mode of CH_4 and CD_4 in the gas phase[2] and for the ν_4 C−H wagging mode of haloforms in both the gas and solution phases.[3,4] Polyatomic linear molecules have degenerate bonding modes with unique angular momentum consequences that also lend themselves to MVCD analysis. That is the topic of this article.

The acetylene molecule, though a linear tetra-atomic, constitutes a spectroscopically complex system that has been extensively explored in a number of laboratories by means of high-resolution spectroscopy.[5] Because of its linearity, vibrational and rotational motions cannot be separated even in the simplest model of its molecular Hamiltonian.

In a previous report,[6] the rotational *g*-values for the ground $\Sigma_g{}^+$ state and for several excited $\Sigma_u{}^+$ fundamental and combination states of acetylene and its deuterated isomers were determined using the RR MVCD technique and were compared to previous ground state determinations from molecular beam magnetic resonance methods. Degenerate transitions were not addressed in that work, although acetylene has both Π_g and Π_u C−H bending fundamental modes, ν_4 and ν_5, respectively, of which the latter is IR-allowed.[7,8] The IR absorption frequency for the ν_5 mode of acetylene is about 750 cm^{-1}, which is very close to the lower frequency limit (700 cm^{-1}) of our spectrometer as well as to the limit of the current technology for vibrational circular dichroism (VCD) measurements.[9] Nevertheless, as shown in this paper, the first evaluation of the vibrational *g*-value of the ν_5 mode of acetylene can be made using its RR MVCD, even under these restricted conditions. This is also the first quantitative determination using MVCD of a vibrational *g*-value for any linear molecule. Such a result was dependent on developing a theoretical model to relate the vibrational *g*-value to the RR MVCD observables as described in the next section.

Theory

Formal representation of the total angular momentum and consequently the observed magnetic moment for excitations to this two-dimensional isotropic harmonic oscillator requires that its vibrational angular momentum must be coupled with the rotational and nuclear angular momenta. Acetylene rovibrational wave functions used in the symmetrized Wang form[5] can be written as

$$|e\rangle = 2^{-1/2}(|v_5 l_5\rangle - |v_5 - l_5\rangle)|JM\rangle \qquad (1)$$

$$|\mathrm{f}\rangle = 2^{-1/2}(|v_5 l_5\rangle + |v_5 - l_5\rangle)|JM\rangle$$

where v_5 and l_5 are the degenerate ν_5 bending mode vibrational quantum numbers, v_5 being the conventional total number of quanta excited and l_5 determining the projection of the vibrational angular momentum on the molecular axis ($l_5 = -v_5, -v_5 + 2, ..., v_5$). In these wave functions, $\mathbf{J}$ is the total angular momentum, $\mathbf{J} = \mathbf{R} + \boldsymbol{l}_5$, where $\mathbf{R}$ is the rotational angular momentum, and *M* is the projection of $\mathbf{J}$ onto the direction of the magnetic field, $\boldsymbol{B}$, $M = -J, -J + 1, ..., J$. For the MVCD experiment, $\boldsymbol{B}$ is collinear with the direction of light propagation. Transitions to the *f*-states from the ground *e*-state are forbidden for the P- and R-branches and allowed for the Q-branch.[7] The energy levels of the molecule without an external field have been parametrized previously,[8] so in order to simulate the MVCD, only the molecular Zeeman perturbation terms need to be added.

The molecular magnetic moment associated with the total angular momentum is given by

$$\mathbf{m_J} = g_J \mu_N \mathbf{J}/\hbar \qquad (2)$$

where

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[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

0022-3654/96/20100-2062$12.00/0

$$g_J = g_R + l^2[J(J+1)]^{-1}(g_v - g_R) \qquad (3)$$

is the molecular (dimensionless) g-value,[6] μ_N is the nuclear magneton, g_R is the rotational g-value, g_v is the vibrational g-value, and l is the vibrational angular momentum quantum number corresponding to ***l***. Figure 1 shows the coupling scheme for the angular and magnetic moments. Only the projection of the total magnetic moment **m** on **J** is well-defined. Nuclear moments are not coupled to **J**, to a good approximation. Nevertheless, the nuclear part of the molecular wave function determines which are the symmetry-allowed rotational states, since the complete molecular wave function must belong to the totally symmetric representation. Note that for large values of J, $g_J \rightarrow g_R$, since, for excitation of the ν_5 fundamental, $l^2 = 1$.

The energy for each state under the Zeeman perturbation is

$$\epsilon_{JlM} = \epsilon_{Jl} - g_J \mu_N M B \qquad (4)$$

where ϵ_{Jl} is the rovibrational energy[5,8] and M is the projection of J into the direction of the magnetic field, $\boldsymbol{B}$. A general theory of RR MVCD is available separately.[1] The ν_5 bending mode has a transition dipole moment pointing perpendicular to the molecular axis C≡C. Thus the absorbance for a $(v''J''M'') \rightarrow (v'J'M')$ transition for the left (+) and right (−) circularly polarized light is given by

$$A_\pm = \kappa\mu^2 |\langle 1\ \pm 1 J'M' | J''\ M''\rangle|^2 |\langle J''011|J'1\rangle^2 \times \exp(-\epsilon_{J''0M''}/kT) \qquad (5)$$

where μ is the vibrational electric dipole transition moment; J'', M'', and J', M' are the quantum numbers for the ground and excited states, respectively; $\epsilon_{J''0M''}$ is the energy of the ground state; k is the Boltzmann constant; T is the temperature; g_I is the nuclear statistical factor, $g_I = 1$ for even J's and $g_I = 3$ for odd J's; and κ is a constant independent of frequency. Symbols in brackets denote the usual Clebsch−Gordan coefficients. The MVCD intensity pattern can be simulated using eq 5 by summing over the line shape broadened contributions from all M components placed on their appropriate Zeeman-shifted frequencies, since the splitting of M levels is too small to be directly monitored under our experimental conditions.

As shown earlier,[1] by moment analysis of the experimental MVCD and absorption line shapes corresponding to a resolved $J'' \rightarrow J'$ transition, an effective g-value, g_e, can be obtained which can be related to the molecular g-values of the ground and excited states by

$$g_e = g_{J'} + 0.5(g_{J'} - g_{J''})c \qquad (6)$$

where $c = -1$ for the Q-branch, $c = J''$ for the R-branch, and $c = -(J'' + 1)$ for the P-branch. Taking into account that $g_{J''} = g_{R''}$ for the ground state and setting $l^2 = 1$ for the excited state, eq 3 can be substituted into eq 6 and rearranged into

$$g_v = g_{R'} + 2(g_e - g_{R'})J'(J'+1)(2+c)^{-1} - c(g_{R'} - g_{R''})J'(J'+1)(2+c)^{-1} \qquad (7)$$

so the vibrational g-value, g_v, can be determined by a moment analysis of the experimental spectrum which yields g_e,[1] combined with knowledge of g_R from the ground state or MVCD of other transitions, for example, $\Sigma_g^+ \rightarrow \Sigma_u^+$.[6] As an approximation, we can set $g_{R'} = g_{R''}$, which further simplifies eq 7 by eliminating the last term.

Experimental Section

The MVCD spectra were recorded with a Fourier transform (FT) VCD instrument based on a commercial FTIR (Digilab FTS-60A) incorporating a superconducting magnet (Oxford Instruments) which provides a magnetic field of 8 T. The details of this instrument have been discussed previously;[9−12] the only change that has been made from our previously published experimental setup is the upgrade of the interferometer to an FTS-60A to allow dynamic alignment, 0.1 cm^{-1} resolution, and step-scan.[11] The improvement in resolution from our previous measurements at 0.5 cm^{-1} resolution resulted in enhanced signal levels and allowed better isolation of overlapping bands but naturally required much longer scan times and a smaller aperture. Thus signal-to-noise ratio (S/N) is a problem for low g-value transitions and is greatly exacerbated in the ν_5 band discussed in this paper because the frequencies approach the far-IR region. The polarization modulation optical setup used for the low IR frequency (<900 cm^{-1}) MVCD measurements reported here includes a ZnSe-substrate grid polarizer, a ZnSe photoelastic modulator, a ZnSe focusing lens, and a liquid nitrogen cooled, narrow band MCT detector. [While this detector's spectral response is not optimal for the ν_5 transition, its S/N was so much higher than that of our wide band MCT detector that we chose to focus just on the R-branch and obtain the best possible S/N.] The optics were generally single layer, AR coated to enhance transmission at 10 μm, which does improve response in the region studied here. The main limitation on spectral range is the ZnSe modulator material, which dictated the choice of all the other optics.

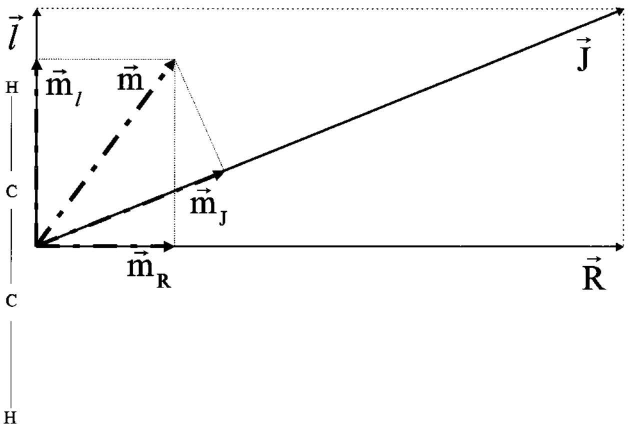

Figure 1. Coupling scheme for C_2H_2 angular momenta: **J**, total angular momentum; **R** and ***l***, rotational and vibrational angular momentum, respectively; **m**, molecular magnetic moment; $\mathbf{m}_l$ and $\mathbf{m}_R$, vibrational and rotational magnetic moment, respectively; $\mathbf{m}_J = g_J\mu_N\mathbf{J}/h$.

C_2H_2 was obtained from AGA Gas, Inc. (as a mixture of acetylene and acetone) and further purified in a glass vacuum system by trapping the acetone with a dry ice bath. The sample was transferred into a brass cell at a pressure of about 2 Torr. The cell was sealed with two KBr windows separated by 6.2 cm and tilted by 5° from parallel, to suppress reflective multipass interference between the windows which can degrade the baseline. No residual spectral features for acetone were observed in the IR absorption spectra we have measured for acetylene. The frequencies and assignments for all the rotational transitions observed here for the ν_5 fundamental band of acetylene matched those available in the literature.[13]

MVCD spectra were scanned in both positive and negative fields, ±8 T, to eliminate artifacts and improve the S/N. Spectra were obtained as an average of eight blocks (four blocks for each direction of the magnetic field) of 1024 rapid scans (moving mirror speed of 0.6 cm/s). The entire data collection took about 20 h. Both the infrared absorption and MVCD spectra were measured at a nominal resolution of 0.1 cm^{-1}, which was subsequently degraded by triangular apodization to

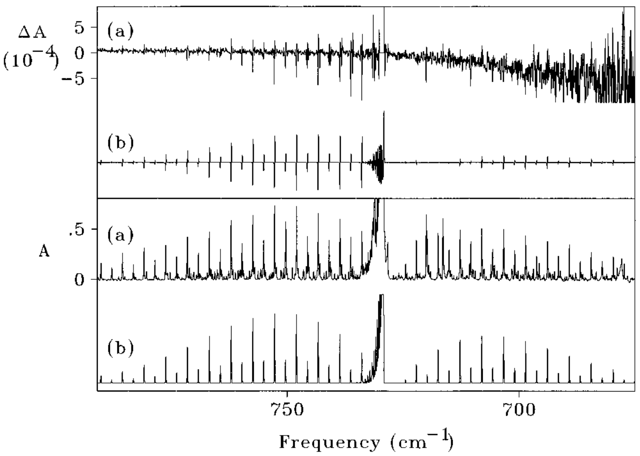

Figure 2. Experimental (a) and simulated (b) MVCD (top) and absorption (bottom) spectra for the ν_5 fundamental mode of C_2H_2. $g_v = 0.5$ and $g_{R''} = g_{R'} = 0.049$ were used for the simulation.

minimize the side bands. The resulting full width at half height (fwhh) for the observed absorbance transitions averages 0.12 cm^{-1}. Phase correction utilized a transferred phase file and determination of the zero path difference from a fiducial mark created with a technique using a second detector as previously described.[10] These phase corrections were designed for the mid-IR and may not be optimized for the lower frequencies studied here, but they offer the best correction that can be made at the current time. Spectra were calibrated using our usual birefringent plate-polarizer pseudo-sample technique,[9] were corrected for the field profile over the sample cell, and were normalized to 1 T for presentation and analysis.

Results and Discussion

Figure 2 shows the overall measured and simulated MVCD and absorption spectra for the ν_5 band of C_2H_2. The experimental RR MVCD for the P-branch is, unfortunately, not usable, because of the noise caused by the intensity loss due to ZnSe absorption and detector sensitivity falloff. In addition, due to the difference between the ground and excited state g-values (see eq 6), the MVCD signal for the P-branch is smaller than that for the R-branch, as can be seen more clearly from the simulated spectrum. Added complications arise from the overlap of the v_5 fundamental transition with other acetylene rovibrational transitions, in particular the $\nu_4 \rightarrow \nu_4 + \nu_5$ hot band. Fortunately, despite the modest S/N, the MVCD spectrum of a substantial part of the R-branch could be measured and resolved, up to a J value of about 18, but only about three transitions of the P-branch can be identified in this spectrum. The error of the RR MVCD intensities for higher J's increases rapidly, resulting in relatively large variations in the moment analysis results above $J = 10$. The values given in Table 1 are for only those low-J R-branch transitions for which the g_e-values were judged to be the most reliably measured. The large variations for the g_v-values derived from these moment analyses are due to the limited S/N of the experimental MVCD spectrum and the spectral overlap with other transitions. The frequencies of the ro-vibrational transitions studied are very close to the cutoff frequencies (700 cm^{-1}) of our spectrometer, making the optimal S/N achievable in this region significantly lower than is normally obtained in the mid-IR region (900−1600 cm^{-1}). The R-branch MVCD transitions appear to be distorted A-terms. Some of this distortion may be due to the inadequacies in the phase correction, but our tests indicate that small phase errors have minimal effect on the A_1/D_0 values obtained from the moment analysis.[12] The spectral shape of the Q-branch MVCD is severely distorted due to its high absorbance in this spectrum, which results from the overlap of adjacent $\Delta J = 0$ transitions, and offers no useful MVCD information. By contrast, for the absorption spectrum, all three branches could be recorded with a reasonable S/N, for J up to about 25.

TABLE 1: Moment Analysis Results of Selected RR MVCD Transitions

branch(J'')	ω^a	$\langle A\rangle_0$ (10^{-4})	$\langle \Delta A\rangle_1$ (10^{-9})	$g_e{}^b$	$g_v{}^c$	$g_{v'}{}^d$
R(1)	733.86	1.120	−5.962	0.105	0.271	0.277
R(2)	736.21	0.819	−5.578	0.134	0.558	0.576
R(3)	738.56	1.413	−11.74	0.163	0.964	0.972
R(5)	743.26	1.550	−5.429	0.046	0.287	0.377
R(6)	745.61	0.846	−2.556	0.059	0.194	0.269
R(7)	748.07	1.440	−5.326	0.073	0.428	0.537
R(9)	752.78	1.568	−6.374	0.080	0.666	0.861
average^e					0.48(25)	0.55(26)

[a] Frequency in cm^{-1}. [b] Apparent g-factor, obtained by a moment analysis of the experimental spectra. [c] The vibrational g-values were calculated using $g_{R'} = 0.049\,03 = g_{R''}$, according to eq 7. [d] The vibrational g-values were calculated using $g_{R'} = 0.052$ and $g_{R''} = 0.049\,03$, according to eq 7. [e] Seven bands with the most reliably determined moments were taken.

Despite the obviously limited S/N of these experimental data, the g_e-values obtained for the lowest eight transitions of the R-branch (Table 1) are significantly larger than the ground state (rotational) g-value. This indicates a substantial vibrational g-factor contribution to the molecular Zeeman effect. As shown in Table 1, the vibrational g_v was calculated from g_e for each of these R(J) transitions according to eq 7, assuming that the established molecular beam magnetic resonance value of g_R (+0.049 03) was applicable for both the ground and excited state rotational g-values.[14] Use of eq 7 to decouple the rotational and vibrational g-values should remove the J-dependence from the g_v contribution and allow improvement of its statistical reliability by averaging over the transitions measured. Since our high-J-value g_e determinations are poor, confirmation of this theoretical point of view is difficult. The average value of g_v determined in this manner for these most reliable low J-transitions was 0.48(25), or roughly 10 times larger than g_R in the ground state. While the uncertainty is certainly high, the change in effective g-value due to the g_v contribution is well in excess of our error limits. Thus this study provides the first quantitative determination of g_v via a RR MVCD experiment.

Previously, we have reported a significant difference between the rotational g-values for the ground state and the ($\nu_4 + \nu_5$) combination mode of acetylene.[6] To estimate the influence of the rotational g-values in this determination, we recalculated g_v using $g_{R''} = 0.049$ and $g_{R'} = 0.046$. [$g_{R''}$ is the known ground state rotational g-value. The MVCD determined change in g-value for the $\nu_4 + \nu_5$ combination mode was $\Delta g_R = -0.0061$,[6] which we attribute to contribution from both bending mode excitations. This prompted us to use the approximation $g_R'(\nu_5) \cong 0.5(g_{R'}(\nu_4 + \nu_5) + g_{R''}(0))$.] The resulting vibrational g-value with these altered g_R parameters was 0.55(26), implying that $g_{R''} \neq g_{R'}$ results in no significant change as compared to the error.

To visualize the effect of the vibrational magnetic moment on these spectra and to offer an alternative method of determination of g_v, we have simulated the RR MVCD spectra of the v_5 mode of C_2H_2 using $g_v = 0.0$, 0.5, and 1.0, as shown in Figure 3 for the transitions of the P- and R-branches. Unfortunately, the unfavorable S/N in the experimental spectrum, particularly for the P-branch, does not allow us enough accuracy to determine g_v based on the direct comparison of simulated

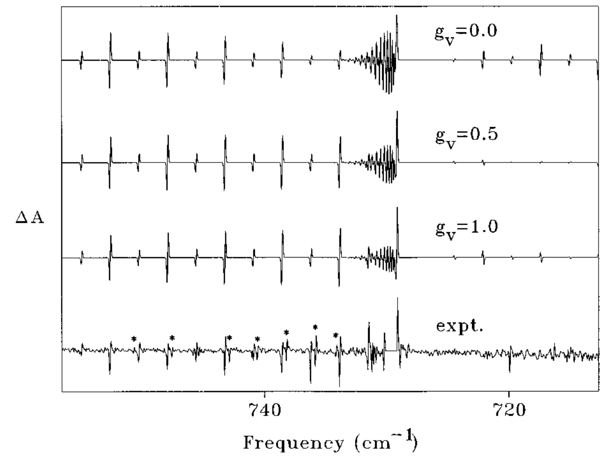

Figure 3. Dependence of the MVCD band shapes for low-*J* transitions on the vibrational magnetic moment. All calculations used $g_{R''} = g_{R'} = 0.049$ and varied g_v over the range from 0.0 to 1.0, as indicated in the figure. Stronger bands that were assigned to transitions other than components of the ν_5 fundamental are marked by asterisks.

and experimental intensities. Nevertheless, the $g_v = 0.5$ value closest to that obtained by moment analysis gives a reasonable spectral pattern. The profiles obtained with $g_v = 0.0$, on the other hand, have much more P-branch intensity than is reasonable, as compared to our experimental data; and those with $g_v = 1.0$ have a sign reversal for the low-*J* P-branch transitions for which we have no experimental evidence. Comparison of the R-branch profiles of the RR MVCD might favor a larger g_v value than found with moment analysis, but such a determination would still lie within its ample uncertainty limits. Thus comparison with the simulated MVCD can be seen to be consistent with our moment analysis determined value of $g_v = 0.48$.

It would be interesting to compare the MVCD determined value for the g_v of the ν_5 mode of acetylene with that from a microwave experiment, but this is clearly not possible due to acetylene's lack of a permanent dipole moment. Vibrational *g*-values of the dipolar HCN and OCS molecules have been determined using such techniques by analyzing the *l*-type splitting of the excited bending modes.[15] Recently, a similar analysis was done for the ammonia bending mode.[16] The vibrational *g*-values for the hydrogen bending modes are positive in both cases (g_v = 0.95 and 0.38 for NH_3 and HCN, respectively), in accordance with our observations for C_2H_2. Since a rotational movement of a proton around the molecular axis should give rise to a *g*-value of 1 for a linear molecule, a substantial nonadiabatic electronic contribution to the magnetic moments of HCN and C_2H_2 is expected, as has been predicted by a theoretical analysis.[17]

Acknowledgment. This work was supported in part by grants from the National Science Foundation (INT 91-07588) and by a University of Illinois Senior Scholar Award (to T.A.K.); P.B. is additionally supported by grants from the Grant Agency of the Czech Republic (GA 203/93/0714 and GA 203/95/0105), and C.N.T., by a Dean's Scholar Fellowship and the Philip L. Hawley Fellowship from the University of Illinois at Chicago.

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JP9525548