

The bending vibration of FeD₂ at 226 cm⁻¹, detected by far-infrared laser magnetic resonance spectroscopy

Helga Körsgen^{a)} and Kenneth M. Evenson

National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303

John M. Brown

Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom

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We report the first gas phase observation of a bending vibration in an open shell molecule by far-infrared laser magnetic resonance. The spectrum is due to FeD₂; its observation shows that rovibrational transitions can be detected with such a spectrometer. The molecule was produced in the reaction between deuterium atoms and iron pentacarbonyl. FeD₂ has a linear ⁵Δ ground state and shows the effects of Renner–Teller coupling in the excited vibrational (010) level. © 1997 American Institute of Physics. [S0021-9606(97)03627-1]

Using a far-infrared laser magnetic resonance (FIR LMR) spectrometer we have detected resonances near 226 cm⁻¹ which belong to the fundamental bending vibration (ν_2) of FeD₂. This represents not only the first gas phase spectrum of FeD₂ but also the first detection of a vibration–rotation transition in the far-infrared spectral region which involves an open shell molecule. Previous FIR LMR experiments have detected either rotational or fine structure transitions. In addition, our measurements permit an interesting spectroscopic study of the Renner–Teller effect occurring in a molecule in a Δ electronic state.

The spectral region between 100 and 400 cm⁻¹ is especially interesting because it embraces many bending vibrations; it is, however, difficult to access with currently available techniques. Infrared sources such as lead salt diode lasers do not operate below 400 cm⁻¹. On the other side of this region, although there is a plentiful supply of far-infrared (FIR) laser lines below 100 cm⁻¹, there are very few which have been characterized above this wave number. In recent years there has been strong development of short wavelength FIR lasers, especially in methanol and hydrazine pumped by infrared CO₂ laser radiation.^{1–3} When combined with a high sensitivity technique such as laser magnetic resonance, the possibility of detecting vibration–rotation transitions of molecules in the gas phase is opened up. At the moment, the shortest wavelength obtainable in our spectrometer is 35.97 μm (278 cm⁻¹).

Vibration–rotation transitions of several closed shell species have already been recorded in the FIR using laser based methods, although all at longer wavelengths. The great majority of these are vibration–rotation tunneling transitions in weakly bound complexes.^{4,5} The only chemically bound molecule for which a FIR vibrational transition has been observed is C₃, for which the bending vibration fundamental band at 63.1 cm⁻¹ was measured.⁶ The earliest of these experiments used fixed frequency lasers and Stark tuning,⁷ but

more recent measurements have been made with tunable sideband spectrometers.⁸

FeD₂ has been detected previously in matrix studies of the dihydrides of iron,^{9–11} and wave numbers of the antisymmetric and bending vibrations have been measured. Related theoretical investigations of the electronic structure^{12,13} suggest that the molecule has a linear ⁵Δ_g ground state. Consequently, it has no permanent electric dipole moment and therefore does not have a detectable rotational spectrum. A recent study of the antisymmetric stretching vibration of FeH₂ in the infrared spectral region by LMR spectroscopy¹⁴ is the first gas phase spectrum of this molecule. It gave a set of molecular parameters and confirmed the theoretical prediction of the ground state. It also provided the stimulus for the present work. Since the bending frequency of FeH₂ is, at 325 cm⁻¹, outside the present operating range of our FIR spectrometer, we have studied FeD₂ instead.

FeD₂ is linear in its ⁵Δ vibronic ground state and can be described with an effective Hamiltonian operator using a Hund's case *a* basis set. Since the ground state is inverted, the lowest spin component is ⁵Δ₄. When one quantum of the bending vibration is excited ($\nu_2 = 1$), two unique vibronic levels are formed through the coupling of the vibrational angular momentum **G** with the orbital angular momentum **L**. The vibronic levels are then characterized by the coupled momenta, ^{2S+1}K_P, where $K = \Lambda + l$ and $P = K + \Sigma$, $l = \pm 1$. In the case of FeD₂, the unique vibronic levels are ⁵Π and ⁵Φ, with lowest spin components ⁵Π₃ and ⁵Φ₅, respectively. Figure 1 shows the vibronic energy levels of the (000) and (010) levels of FeD₂; the effects of spin-orbit coupling have to be superimposed on this scheme. The separation between the two unique levels is given by $g_K \cdot \Lambda \cdot \Delta K$.¹⁵ The value for g_K is not known, but it probably has a magnitude of a few wave number units, judging from other molecules.¹⁶

For our measurements, we used a FIR LMR spectrometer in an intracavity configuration. The details of the spectrometer have been given elsewhere.¹⁷ The FIR radiation originates from a methanol laser pumped by an infrared CO₂ laser. FeD₂ was produced inside a 2-T magnet using a microwave discharge of 2450 MHz running at 60 W in 133

^{a)}Present address: Institut für Angewandte Physik, Wegelerstraße 8, D-53115 Bonn, Germany.

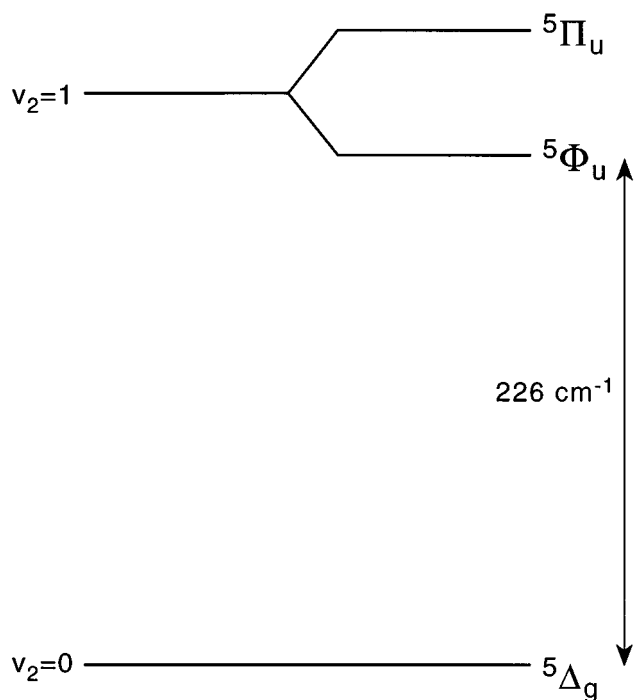


FIG. 1. The energy level diagram of the vibronic components of the levels (000) and (010) of FeD_2 . In the upper ($\nu_2 = 1$) level the effect of coupling of vibrational angular momentum and orbital angular momentum leads to two unique vibronic states. In all these states, there is an additional splitting due to spin-orbit coupling which is not shown in this diagram. There are also significant contributions to the positions of the spin-orbit components from the rotational constant (B) and the spin-rotation constant (γ).

Pa (1 Torr) of helium and 13.3 Pa (0.1 Torr) of deuterium. Traces of $\text{Fe}(\text{CO})_5$ were added downstream in the absorption region and did not pass through the discharge. The production conditions were similar to those used to generate the FeH radical.¹⁸ The signals were modulated at 39 kHz with Zeeman modulation coils and recorded using a Ga:Ge photoconductor detector. They were amplified by a lock-in amplifier using 1- f detection.

We have detected several spectra which are attributable to FeD_2 , as well as other signals not yet assigned but probably belonging to further FeD_2 transitions or, possibly, fine structure transitions in FeD . Table I gives a summary of laser

TABLE I. Summary of measured laser lines and assigned transitions observed in the ν_2 fundamental band of $^{56}\text{FeD}_2$ by FIR laser magnetic resonance.

FIR laser line		Lasing gas	Pump	FeD ₂ transition	
μm	GHz			$^5\Pi_3 \leftarrow ^5\Delta_4$	$^5\Phi_3 \leftarrow ^5\Delta_2$
39.924	7509.0362 ^a	CH ₃ OH	9P34	R(6)	
41.355	7249.2660	CD ₃ OH	10R18		
41.871	7159.8953	CH ₃ OH	9P16		
43.697	6860.6642	CD ₃ OH	10R18	<i>Q</i> branch	
43.781	6847.4732	CH ₃ OH	10R36		
44.245	6775.7835	CH ₃ OH	9P16		<i>Q</i> branch
46.165	6493.9115	CH ₃ OH	9P10	<i>P</i> (4)	
46.793	6406.7929	CH ₃ OD	9P52	<i>P</i> (5)	

^aThe measured laser frequencies have a fractional uncertainty of 2×10^{-7} .

lines on which resonances have been observed and the assignments of some of the signals to transitions in FeD_2 . So far, we have assigned one transition in the $^5\Pi_u(010) \leftarrow ^5\Delta_g(000)$ system and another one in the $^5\Phi_u(010) \leftarrow ^5\Delta_g(000)$ system. Figure 2 shows a part of the spectrum arising from *Q*-branch transitions between the lowest spin components of both states involved ($^5\Pi_3 \leftarrow ^5\Delta_4$). The resonances do not show the typical *Q*-line pattern expected when $\Delta g_J = 0$; this is because the additional vibrational angular momentum in the upper state changes the effective g factor for a given rotational state with respect to its value in the lower state. In addition to the *Q*-branch resonances with $J = 4$ to 8 in the $^5\Pi_3 \leftarrow ^5\Delta_4$ subband, we have detected one *R* and two *P* lines. We have performed a least squares fit on these data with an effective Hamiltonian operator using a $^5\Delta$ basis set to describe the ground state and a $^5\Pi$ basis set for the upper state, from which we obtain values for ν_0 , B_0 , and α_B . Table II lists the fitted values and a comparison with the corresponding parameters in the matrix studies and isotopically scaled parameters from the mid-infrared LMR study of FeH_2 .¹⁴ Since we have assigned only *Q* lines in the $^5\Phi_3 \leftarrow ^5\Delta_2$ vibronic subband, we cannot determine an accurate value for the rotational constants in these states; it is nevertheless possible to fit the measurements with the effective Hamiltonian; see Table II. From the large change in the centrifugal distortion constant D on vibrational excitation, we can determine an approximate value for g_K . We determine g_K to be about -0.92 cm^{-1} ; this means that the $^5\Phi$ state lies about 3.68 cm^{-1} below the $^5\Pi$ state.

In the gas phase, a subband origin for transitions between two components has contributions from the vibrational origin, the rotational and spin-orbit coupling terms, and also from the vibronic parameter g_K . In so far as we know these parameters, we have included their effects in our calculation. A comparison of the matrix value of the bending wave number is not straightforward for two reasons. First, the gas phase band origin depends on the value of several quantities which are not yet determined for FeD_2 . The value of ν_0 determined from the fit of the $^5\Phi_3 \leftarrow ^5\Delta_2$ resonances is likely to be the more reliable of the two because all the spin-dependent contributions to the band origin vanish in this case (since the states involved have $\Sigma=0$). Second, it is not clear how many of these contributions are quenched in the matrix, quite apart from the usual matrix effects. If we assume that neither the rotation nor the spin-orbit terms have an effect in the matrix, we should compare ν_0 (226.06 cm^{-1}) with the matrix value (235 cm^{-1}). Even if the spin-orbit term is included, the gas phase value would be essentially the same. The rotational parameters can be compared with the values obtained by isotopic scaling of the corresponding parameters in FeH_2 from Ref. 13. The infrared spectrum of FeH_2 is due to the antisymmetric stretching vibration and gives a value of $\alpha_{B,3}$ rather than $\alpha_{B,2}$. To obtain a value to compare with the FeD_2 results, we have used $\alpha_{B,2} = -1/2\alpha_{B,3}$.

There are four reasons for the assignment of the spectrum to FeD_2 : (i) the matrix values for the vibrational wave number of the FeD_2 bending motion in both xenon⁹ and argon¹⁰ are close to the value obtained by FIR LMR; (ii) the

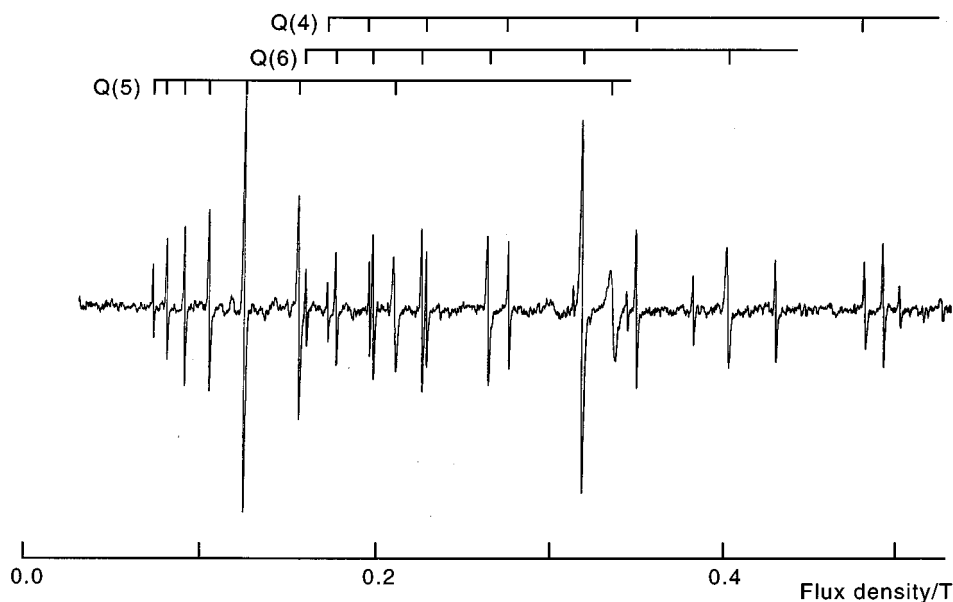


FIG. 2. The laser magnetic resonance spectrum of the Q branch belonging to vibronic component ${}^5\Pi_3 \leftarrow {}^5\Delta_4$ of the ν^2 band of FeD_2 . It was recorded with a CD_3OH laser line at $43.697 \mu\text{m}$ pumped by the CO_2 laser transition 10R18. The spectrum was recorded in parallel (π) polarization ($\Delta M_J = 0$). The assignment of M_J components is indicated in the figure.

rotational parameters are in agreement with the isotopic scaled molecular parameters from FeH_2 ;¹⁴ (iii) the experimental data can be fitted to the expected model by assigning the resonances to two different transitions, ${}^5\Pi_3 \leftarrow {}^5\Delta_4$ and ${}^5\Phi_3 \leftarrow {}^5\Delta_2$; and (iv) the latter spectrum shows K -type doubling with the 2:1 intensity distribution expected from nuclear spin statistics for FeD_2 .

Many resonances in our spectra still await assignment. The transitions within the same vibronic systems but arising from different spin components are expected to occur in the same region. There is also a possibility of detecting fine structure transitions. Since our preliminary analysis shows that the ground ${}^5\Delta$ state is essentially unperturbed, fine structure transitions of FeD_2 would have only magnetic dipole intensity and are therefore expected to be 1–2 orders of magnitude weaker than vibrational transitions. However, FeD is strongly perturbed and could, by analogy with FeH ¹⁹ show very strong fine structure transitions which probably occur within the region covered by our spectra.

TABLE II. Preliminary values of molecular constants cm^{-1} .

Parameter	${}^5\Pi_3 \leftarrow {}^5\Delta_4^a$	${}^5\Phi_3 \leftarrow {}^5\Delta_2^b$	Isotopic scaling ^c	Refs. 9 and 10
ν_2	221.143 21	226.060		232(Xe), 235(Ar)
B_0	1.541 61		1.525 537 5	
$\alpha_{B,2}$	0.013 018	0.0054	0.008 425	

^aParameters determined from a fit of the data assigned to the transition ${}^5\Pi_3 \leftarrow {}^5\Delta_4$ to an effective Hamiltonian.

^bParameters determined from a fit of the data assigned to the transition ${}^5\Phi_3 \leftarrow {}^5\Delta_2$ to an effective Hamiltonian.

^cValues estimated from those of FeH_2 determined in Ref. 14.

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