THE DIPOLE MOMENT OF ⁷LiH IN THE ELECTRONICALLY EXCITED A ${}^{1}\Sigma^{+}$ STATE

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Received 3 July 1980, in final form 22 September 1980

We have measured the dipole moment of ⁷L₁H in several vibrational levels of the A ¹ Σ^+ state. Electric-field-induced quantum beats have been observed after pulsed laser excitation of a single rotational R(0) transition From the beat frequencies obtained for different vibronic states, the following dipole moments were derived $\mu_2 = 1.54(7)$, $\mu_4 = 0.67(4)$ and $\mu_5 < 0.15$ D

1. Introduction

The LIH molecule is the simplest neutral heteronuclear molecule and therefore the subject of numerous experimental [1-3] and theoretical [4-8]investigations. Many properties such as potential energy [4, 5], electronic transition moments and dipole moments and their dependence on internuclear distance have been computed for several electronic states [9]. It is well known that the A ${}^{1}\Sigma^{+}$ states of the alkali hydrides show an anomalous potential curve due to avoided curve crossings [10] Vidal [11] pointed out that the A ${}^{1}\Sigma^{+}$ potential curves of LiH and LID computed by the IPA method differ by 20 cm⁻¹, indicating a breakdown of the Born-Oppenheimer approximation For these reasons we embarked on a long-term program in order to get information on molecular properties of the alkali hydrides LiH, ..., CsH and their isotopic species LID, ..., CsD in excited states. In the case of LiH, theory predicts that the dipole moment of the A ${}^{1}\Sigma^{+}$ state changes sign near the equilibrium distance r_{e_1} marking a switch from Li⁻H⁺ type behaviour at small nuclear separations to Li⁺H⁻ type behaviour when the nuclei are at larger distances, and finally the dipole moment approaches zero when the atoms are well separated. Due to anharmonic vibrations, a strong dependence of the dipole moment on the vibrational level is expected.

In this paper we present values of dipole moments for several vibrational states of the $A^{1}\Sigma^{+}$ state of LiH measured by laser-induced Stark quantum beat spectroscopy (SQBS) [12]. SQBS has several advantages over other Doppler-free methods such as levelcrossing [13] and optical double-resonance [14] methods: corrections due to laser power or rf power, and scanning of the electric field and radio frequency, are not necessary and the quantum beat signals are easy to evaluate with high accuracy. Thus SQBS is a method well suited to determine electric-field splittings in atoms and molecules.

2. Experimental

In a ${}^{1}\Sigma$ state of a heteronuclear diatomic molecule, the Stark splitting of a rotational level J' is given by

$$\Delta W(M'_1, M'_2) = (\mu^2 E^2 / B_v hc) F(J', M'_1, M'_2),$$

$$F(J', M'_1, M'_2) = \frac{3[(M'_1)^2 - (M'_2)^2]}{2J'(J'+1)(2J'-1)(2J'+3)}.$$

J' is the angular momentum in the state considered, $M'_{1,2}$ its projection onto the field direction, and $B_{u'}$ is the rotational constant of the vibrational level u'. For the following reasons it is advantageous to excite a level of low rotational quantum number, preferably a J' = 1 level via an R(0) line: (1) The field strength necessary to perform the experiment increases quadratically with J'.

(2) The coherent part of the signal, i.e. the amplitude of the modulation, decreases rapidly with increasing J'.

(3) In contrast to the Zeeman effect, the splitting of the sublevels depends on the absolute value of the magnetic quantum number M'. Thus for higher J' one obtains a superposition of different beat frequencies, complicating the evaluation.

In the case of R(0) line excitation, only one beat frequency arising from the splitting of the sublevels M' = 0 and $M' = \pm 1$ is observed. The expected signal consists of an unmodulated and a modulated part:

$$I = (I_0 + I_1 \cos \omega t) e^{-t/\tau},$$

with

$$\omega = \frac{3}{10} \pi E^2 \mu^2 / B_{\mu} h^2 c$$

and τ is the excited-state lifetime.

The ratio $S = I_1/I_0$ is essential for the detectability of the quantum beat signal. Results of S computed using the Breit-Franken formula for pulsed excitation [15] of an R(0) line are given in table 1.

Both the exciting beam and the observed fluorescence are polarized at 45° with respect to the field direction. Their propagation vectors form different angles (0° and 135° respectively) to each other. As one can see the most favourable situation occurs when the directions of excitation and observation are collinear. However, for practical reasons an angle of 135° may be preferred. No beat signal is observed at 90°. Excitation with an R(0) line in a ${}^{1}\Sigma^{-1}\Sigma$ molecu-

Table 1

Relative amplitude of the modulations for J' = 1 excitation. The exciting light and observed fluorescence are linearly polarized with the polarization vectors at 45° to the field direction

Excitation	Observation	Angle between exciting beam and observed fluorescence	
		()°	135°
R(0)	R (0)	1	0.94
R(0)	P(2)	0.14	0.1
R(0)	R(0) + P(2)	0.59	0.49

lar transition produces a fluorescence spectrum which appears as a progression of R(0)-P(2) doublets due to the decay into different vibrational levels of the final state. Usually these doublets are not resolved. Thus one gets a superposition of two rotational lines. According to the different Hönl-London factors of these lines, the P(2) transition is twice as strong as the R(0) transition and because of the smaller coherent part in the P(2) line the amplitude of the modulations is diminished significantly.

A LiH molecular beam was prepared by passing H₂ through molten Li in a stainless-steel oven at 1050 K. After leaving the oven through a 1 mm diameter orifice the beam entered a parallel-plate capacitor (plate separation 1.015 cm) in a differentially pumped vacuum chamber which is essentially the same as that described in ref. [13]. The molecules were excited to the (v', 0) progression of the A-X band system by short light pulses from a nitrogenlaser-pumped dye laser oscillator amplifier system. The dye laser oscillator is a two-grating apparatus [16, 17] with one grating used as beam expander. The laser produced an output of 0.1 Å bandwidth continuously tunable over the whole emission region (360-385 nm) of the dye used $(5 \times 10^{-3} \text{ mol/l PBD in})$ toluene).

Molecular fluorescence polarized at an angle of 45° with respect to the field direction was detected by an RCA 1P28 photomultiplier tube. In order to suppress laser stray light, a cut-off filter (Schott KV 408) was placed in front of the multiplier. Laser-induced fluorescence spectra were obtained by scanning the laser frequency and monitoring the resonance fluorescence signal from the PMT with a boxcar integrator (PAR 162). The fluorescence lines were assigned by means of the tabulated lines [3] and a computer program which calculated theoretical spectra from Dunham coefficients. In fig. 1 part of the (2, 0) band in the A-X transition showing the neighbourhood of the R(0) line is shown.

Decay signals following the laser pulse were detected using the technique of delayed coincidences: A time to amplitude converter (TAC) (Ortec 437A) was started by the response signal of a fast photodiode produced by a small part of the laser beam and stopped by the first fluorescence photon detected by the PMT followed by fast electronics (Ortec 454 amplifier and 453 discriminator).



Fig. 1. Excitation spectrum of ⁷LiH in the vicinity of the (2, 0) band head in the A-X system including the R(0) line where the beat experiment was carried out.

TAC pulse-height analysis was done by means of a multichannel analyzer (Ortec 6240B). The pulseheight distribution exhibits the decay curve of the fluorescent molecules. To avoid pile-up effects caused by the accumulation of more than one detected fluorescence photon following the laser pulse, the fluorescence rate should be kept lower than one tenth fluorescence photon per laser pulse. This method is well suited to detect very low fluorescence rates and is furthermore insensitive to fluctuations in laser power and molecule production. The decay curves collected in the multichannel analyzer were transferred to a HP 1000 computer system in order to store and evaluate the signals.

3. Results

A typical decay signal obtained from R(0) line excitation is shown in fig. 2. The field strength was 7.9 kV/cm. The solid line is a computer-fitted curve to the signal corresponding to a dipole moment of 1,54 D and a modulation of 34%. In the case of the



Fig. 2. Quantum beats in the exponential decay of the $A^{-3}\Sigma^+ v' = 2$, J' = 1 state obtained at a field strength of 7.9 kV/cm. The solid line is a computer fit corresponding to a dipole moment of 1.54 D.

v'=5, J'=1 excitation, no beat signal was observed at 20 kV/cm, the present limit of field strength, indicating a dipole moment of less than 0.15 D. Experiments at higher field strength are in progress. Experimental results of dipole moments in the v'=2, 4 and 5 vibrational states are listed in table 2 and compared with theoretical values.

The error limits are determined by the following contributions to the total uncertainty: The error in determining the field strength was 3%. The rotational constants are known within an error limit of 0.1%.

The absolute time calibration is of an accuracy of better than 1%: The time calibration pulse of a pulse generator could be detected with an accuracy of one

Table 2

Comparison of theoretical and experimental dipole moments in the A $^{1}\Sigma^{+}$ state of ^{7}LiH

Vibrational	Dipole moment $\mu_{w'}$ (D)			
quantum number v'	theory [9]	this work $ \mu $	Dagdigian µ	
0	-2.39			
1	-1.97		1.88(19)	
2	-1.47	1.54(7)	1.48(18)	
4	-0.50	0.59(4)		
5	-0.028	< 0.15	0.29(5)	
6	+0.45			

channel while the pulse peak separation was 200 channels Finally the fit error depends on the modulation frequency of the beat signal and is less than 1.5% for the v'=2 and 2.5% for the v'=4 state, respectively

In the case of the $\nu' = 5$ state a dipole moment of 0.15 D should reveal itself at a field strength of 20 kV/cm in a distortion of the exponential decay curve and thus suggesting a significant change of the lifetime, dependent on the polarization of the detected fluorescence This effect was not observed and the value of $\mu_5 = 0.15$ D may be regarded as an upper limit for the dipole moment

4. Discussion

In a ${}^{1}\Sigma$ state the electric-field-induced level splitting of a rotational state is quadratic in μ . Thus the sign of the dipole moment cannot be deduced by this method. The absolute values, however, obtained by SQBS show good agreement with theoretical MC SCF calculations, though there is a tendency to slightly larger values This behaviour is consistent with the fact that the MC SCF potential is shifted to a slightly larger internuclear distance compared to the RKR potential [4], thus lowering the theoretical absolute values for the negative dipole moments Recently Dagdigian has measured the dipole moments of the v' = 1, 2 and 5 states using the technique of electric-field level crossing [18]. The results are shown in the third column of table 2. His measurements show good agreement with our results in the case of the v' = 2 level, whereas his value for v' = 5 is twice as large as the upper limit given in our measurements Accurate measurements of dipole moments in the v' = 5 and v' = 6 levels, where the dipole moment changes sign, as well as in higher excited vibrational states, will be of considerable interest. This should provide an improved test of the theory. These experiments and further measurements of dipole moments in vibrational states of the A Σ^+ state of L₁D are in progress

Acknowledgement

We are indebted to Dr. C R. Vidal for generously providing Dunham coefficients and Franck-Condon factors of the A-X system of LiH and other isotopic species We gratefully acknowledge important contributions by Dr. Hartmut Schweda This work was supported by the Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 161

References

- [1] F H Crawford and T Jorgensen Jr, Phys Rev 47 (1935) 932
- [2] K C Li and W C. Stwalley, J Mol Spectry 69 (1978) 294
- [3] F B Orth and W C Stwalley, J Mol Spectry. 76 (1979) 17
- [4] WC Stwalley, W.T Zemke, KR Way, KC Li and TR Proctor, J Chem Phys 66 (1977) 5412
- [5] K K. Docken and J Hinze J Chem Phys. 57 (1972) 4928
- [6] W T Zemke and W C Stwalley, J Chem Phys 68 (1978) 4619
- [7] W T Zemke, K R Way and W C Stwalley, J Chem Phys 69 (1978) 402
- [8] WT Zemke, J.B Crooks and WS Stwalley, J Chem Phys 68 (1978) 4628
- [9] K K Docken and J Hinze, J Chem Phys 57 (1972) 4936
- [10] R S Mulliken, Phys Rev 50 (1936) 1028
- [11] C R Vidal, private communication
- [12] A Hese, A Renn and H S Schweda, Opt Commun 20 (1977) 385
- [13] G Dohnt, A Hese, A Renn and H S Schweda, J. Chem. Phys 42 (1979) 183
- [14] R F Wormsbacher, S L Lane and D O Harris, J Chem. Phys 66 (1977) 2745
- [15] P Franken, Phys Rev 121 (1961) 508
- [16] M Littmann, Opt Letters 3 (1978) 138.
- [17] I Shoshan, N N Danon and U P Oppenheimer, J Appl Phys 48 (1977) 4495
- [18] P Dagdigian, J Chem Phys, to be published