Transition dipole function and radiative lifetimes for the A and C $^1\Sigma^+$ states of the LiH molecule

Hamid Berriche and Florent Xavier Gadéa

Regular Article

Transition dipole function and radiative lifetimes for the A and C $^1\Sigma^+$ states of the LiH molecule

Hamid Berriche[1,2,a] and Florent Xavier Gadéa[3]

[1] Laboratoire des Interfaces et Matériaux Avancés, Faculty of Science, University of Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia
[2] Mathematics and Natural Sciences Department, School of Arts and Sciences, American University of Ras Al Khaimah, Ras Al Khaimah, UAE
[3] Laboratoire de Physique et Chimie Quantique, UMR 5626 du CNRS, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France

Abstract. The transition dipole moments of the first eight $^1\Sigma^+$ states of the LiH molecule have been calculated using ab initio approach based on the pseudopotential technique. Such transition dipole moments have been used to determine the radiative lifetimes for all vibrational levels of the first and the second excited states, A and C $^1\Sigma^+$, using accurate adiabatic potential energy curves. In addition to the bound-bound transitions, we have included the bound-free emissions probabilities. The latter was calculated exactly and using the Franck-Condon approximation and then included in the total radiative lifetime. A significant change in these lifetimes has been observed, particularly for the higher excited vibrational levels for which the approximate evaluation breaks down. The radiative lifetimes of the vibrational levels of the A$^1\Sigma^+$ exited sate are in very good agreement with the few available theoretical and experimental results. However, the radiative lifetimes associated to the C$^1\Sigma^+$ state are presented here for the first time.

1 Introduction

As a result of their interesting properties, alkali hydrides continue to be the subject of numerous experimental and theoretical studies. There are considerable experimental spectroscopic information and theoretical investigation on the lithium hydride molecule [1–40]. The evaluation of the radiative lifetimes of diatomic molecules is of great interest from the experimental and theoretical point of view. LiH is the simplest heteronuclear molecule. Many ab initio and dynamical studies have been performed in order to determine: (i) the potential energy and the spectroscopic properties of many electronic states, and (ii) to test developed methods and techniques studying the nonadiabatic effects such as the adiabatic correction, the radial coupling, the vibronic shifts and predissociation. Wine and Melton [38] have measured the radiative lifetimes of the vibrational levels $v = 5$ and 8 of the first excited state (A$^1\Sigma^+$); while Dagdigian [37] has measured the same quantity for $v = 2$, 5 and 7. In another work Dagdigian [34] has measured the vibrational dependence of the A$^1\Sigma^+$ dipole moment. Theoretically, Zemke et al. [35] have determined the radiative lifetimes of all bound vibrational levels of the A$^1\Sigma^+$ state, while Partridge et al. [1] have reported values for only the four first levels. The radiative lifetimes of the vibrational levels of the C$^1\Sigma^+$ state were not measured or predicted previously. Recently, an optical-optical dou-

ble resonance experiment on LiH molecule [40] has been done in order to estimate the nonradiative lifetimes of the C$^1\Sigma^+$ vibrational levels. In this study the authors calculated the radiative lifetime of these vibrational levels but no values were presented in their paper. Therefore, the radiative lifetime of the vibrational levels of the C$^1\Sigma^+$ state will be addressed here for the first time. A particular focus will be on the bound-free contribution in C-X $^1\Sigma^+$ and C-A $^1\Sigma^+$ transitions.

In a previous studies [10] we have determined the potential energy curves for nearly all the adiabatic and diabatic $^{1,3}\Sigma^+$ states dissociating into Li ($2s$, $2p$, $3s$, $3p$, $3d$, $4s$ and $4p$) + H ($1s$) for a range of internuclear distances varying from 1.8 to 30 a.u. These data have been improved later for a wide range of internuclear distances varying from 1.8 to 200 a.u. In addition, we have computed their adiabatic and diabatic permanent and transition dipole moments. In our calculation we have used an ab initio treatment based on pseudopotential, operatorial core valence correlation and full CI with an efficient diabatisation procedure [10,41]. The adiabatic and diabatic permanent dipole moments of the first eight $^1\Sigma^+$ states have been presented as function of the internuclear distance R; they illustrated the ionic character of these states. The high accuracy of these data has been demonstrated by the evaluation of the radial coupling [10], the adiabatic correction [14], the vibronic shifts [13], and the nonradiative lifetimes due to the predissociation of the vibrational

ᵃ e-mail: hamid.berriche@fsm.rnu.tn

levels of $A^1\Sigma^+$ [12] and $C^1\Sigma^+$ [15] states. The aim of the present work is to use these accurate adiabatic potential energy curves and the adiabatic transition dipole moments in order to calculate the radiative lifetimes of all vibrational levels trapped in the $A^1\Sigma^+$ and $C^1\Sigma^+$ states of the LiH molecule. For the C state, the nonradiative lifetimes were shown to present very important variations, ranging from nanoseconds to microseconds [15]. Radiative life times are expected to present smoother variations, however it is important to estimate them accurately in order to point out the dominant contribution. In a very recent study devoted to the LiH^+ molecule [42], it was shown that similar pseudopotential approaches [43] can predict the vibrational spacing with an accuracy about the wavenumber.

The paper is organized as follows. In Section 2 we, briefly, present a summary of the method and give numerical details. Section 3 is devoted to the presentation and discussion of the calculated adiabatic transition dipole moment and the derived radiative lifetimes for nonrotating molecule ($J = 0$). Finally, we summarize our work in Section 4.

2 Summary of the method

In this section we present a brief description of the method of calculation of the radiative lifetime based on the Golden Rule approximation. Given a vibrational level of an excited electronic state ($A^1\Sigma^+$ for example), two possible transitions can occur, bound-bound and bound-free transitions. The radiative lifetime of a vibrational level v' corresponding to only bound-bound transitions is given by:

$$\tau_{v'}(\text{bound-bound}) = \frac{1}{\Gamma_{v'}(\text{bound-bound})}$$

where

$$\Gamma_{v'}(\text{bound-bound}) = \sum_{v=0}^{nv} A_{vv'}, \qquad (1)$$

where $A_{\nu,\nu'}$ is the usual Einstein A coefficient linking for example the $A^1\Sigma^+(v')$ and $X^1\Sigma^+(v)$ levels if we are concerned with the $A^1\Sigma^+$ radiative transitions. Once all the necessary A Einstein coefficients are calculated, their summation according to equation (1) gives the radiative lifetimes, which can be eventually compared to the available experimental and theoretical results. In our calculation the integration is performed on a dense grid varying between 1.8 and 50 a.u. At smaller distances than 1.8 a.u, the transition dipole moment is taken to be a constant equal to the dipole moment at the distance $R = 1.8$ a.u, while the potential energy curves of the X, A and C $^1\Sigma^+$ states were extrapolated using a repulsive exponential form. Although Q lines are forbidden here, rotational effects will not be considered in the present work.

It has been shown previously by Zemke et al. [35] that there is a missing contribution in the radiative lifetime given by equation (1). It is related to the bound-free transitions, which is more significant for the higher vibrational

levels close to the dissociation limit of the excited electronic state, here the continuum radiation to state above the dissociation limit of the ground state. It corresponds therefore to the contribution of the bound-free transition missing in equation (1). It is related to the transition between the vibrational level v', which belongs to the excited electronic state, to the continuum of the ground state or the lower state in general. Such contribution is not negligible as it was demonstrated by Partrigde et al. [1] and Zemke et al. [35]. It is more important for the higher vibrational levels due the difference of the location of the wells. The bound-free emission has been also discussed previously by Stephan and Dalgarno [44] for the hydrogen molecule. The evaluation of this term has shown its importance in a recent work for the $C^1\Pi_u$ state of H_2 [45,46].

This missing term is given by the following equation

$$\Gamma_{v'}(\text{bound-free}) = \frac{64\Pi^4}{3h^4c^3} \int_{E_{as}}^{E_{v'}} E^3 \, ||\langle \chi_E | \mu | \chi_{v'} \rangle|^2 dE \quad (2)$$

where all quantities are expressed in atomic unit.

The total radiative lifetime is thus given by the two contributions, the usual bound-bound (Eq. (1)) and the bound-free (Eq. (2)).

$$\Gamma_{v'} = \Gamma_{v'}(\text{bound-bound}) + \Gamma_{v'}(\text{bound-free}). \qquad (3)$$

On the other hand, to avoid the explicit integral over the continuum, a simpler approximate evaluation was proposed by Zemke et al. [35]. The closure relation of an electronic state composed by vibrational levels and the continuum is given by:

$$\sum_{v=0}^{nv} |\chi_v\rangle \langle \chi_v| + \int_{E_{as}}^{\infty} |\chi_E\rangle \langle \chi_E| \, dE = I. \qquad (4)$$

The projection of a vibrational level $|\chi_{v'}\rangle$ belonging to the higher electronic state gives:

$$FC_{v',cont} = \int_{E_{as}}^{\infty} |\langle \chi_{v'} // \chi_E \rangle|^2 \, dE = 1 - \sum_{v=0}^{nv} |\langle \chi_{v'} \chi_v \rangle|^2. \qquad (5)$$

Using the Franck-Condon approximation proposed by Zemke et al. [35] the bound-free contribution is given by:

$$\Gamma_{v'}(\text{bound-free}) = \frac{64\Pi^4}{3h^4c^3} |\mu(R_{v'+})|^2 \, FC_{v',cont} \nu_{v',cont}^3 \quad (6)$$

where $\nu = E_{\vartheta'} - E_{as}$ is the energy difference between the vibrational level v' and the energy of the asymptotic limit to which belongs the continuum.

$\mu(R_{v'+})$ is the transition dipole moment at the right external turning point.

In this study we will calculate the bound-free contribution exactly and using the approximation proposed by Zemke et al. [35]. We will study the radiative lifetimes of the A and C $^1\Sigma^+$ excited states.

The bound and continuum states and the vibrational levels were determined by means of the Numerov algorithm. However, a first trial set of approximate energy levels have been determined by diagonalizing a tri-diagonal
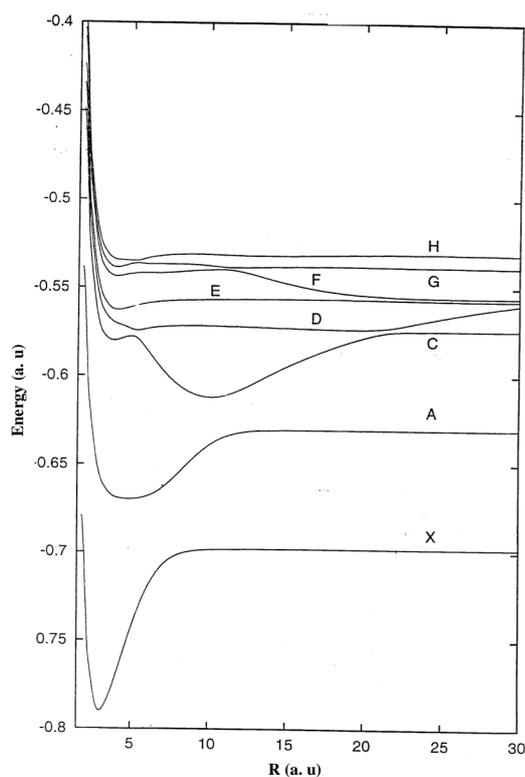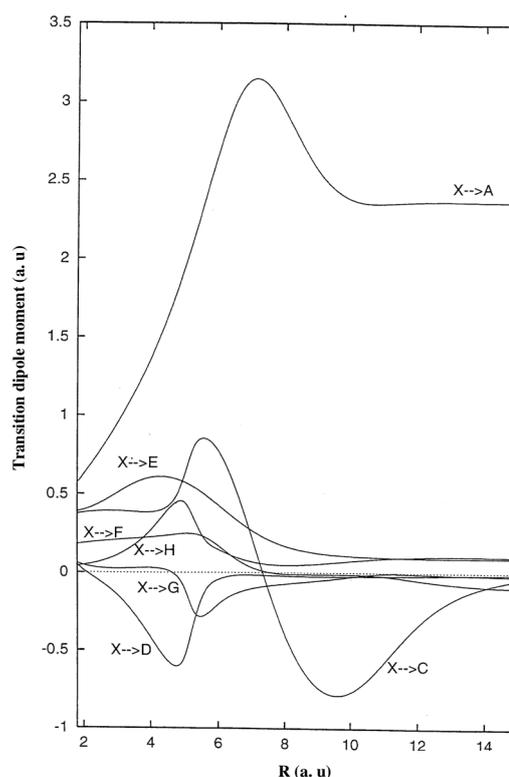
Fig. 1. Potential energy curves of the eight lower $^1\Sigma^+$ states named X, A, C, D, E, F, G and H dissociated into Li (2s, 2p, 3s, 3p, 3d, 4s and 4p).

Fig. 2. Transition dipole moments from the X$^1\Sigma^+$ to the higher $^1\Sigma^+$ states.

matrix and provided to the Numerov propagator. This matrix corresponds to the numerical derivative of the nuclear Schrödinger equation on a radial grid of N points (N is taken larger than the last vibrational level). All used quantities, such as the potential energy curve, the transition dipole moment and the bound and free wave functions, were determined for a radial grid of 30 000 points. The used grid in the integration of the bound-free contribution is of 1000 energy points. Tests were carried out to ensure the convergence of the radiative lifetime for integration on the radial as well as the energy grids.

3 Results and discussion

3.1 Adiabatic potential energy curves and transition dipole moments

Figure 1 presents the adiabatic potential energy curves of the eight lowest $^1\Sigma^+$ states (X$^1\Sigma^+$, A$^1\Sigma^+$, C$^1\Sigma^+$, D$^1\Sigma^+$, E$^1\Sigma^+$, F$^1\Sigma^+$, G $^1\Sigma^+$ and H$^1\Sigma^+$) of the LiH molecule that will be used to determine the radiative lifetimes. The good accuracy of such adiabatic potential energy curves was confirmed by the comparison of their spectroscopic constants (R_e, D_e, ω_e, T_e) with the available works and presented in our previous studies [10]. Some of them were also exploited in dynamical investigations such as the rovibrational distribution [16] of LiH in its ground state and its radiative association. In addition, the used potential energy and the transition dipole moment are extrapolated

at short distances to complete the missed repulsive part of the potential by an exponential form, essentially for the X, A and C $^1\Sigma^+$ states. Such extrapolation is needed to evaluate the contribution of the continuum.

Taking benefit of the related diabatic calculations [10,11], nonadiabatic effects have been thoroughly estimated for the excited states of LiH [12,13,15,47–49] and the latest comparison with experimental results has shown their good accuracy [47,48]. For X and A states, the adiabatic correction is the dominant effect and produces a rather smooth shift of the vibrational levels by a few wavenumbers except for the highest one were the correction deacreases [12,13]. For C and D states, they become somewhat larger and in addition to the smooth shift, for the vibrational levels located in the inner wells ($v = 34$ for C and $v = 2.7$ for D) the vibronic shift is quite larger [15,47–49]. The nonradiative lifetimes have also been investigated [13,15,47–49]. Whereas the individual ones may present strong variations considering or not the adiabatic correction, for example, the global shape of the envelope was found very robust [15]. A similar behaviour can be expected here, some influence of nonadiabatic effects for the individual levels, particularly for $v = 34$ of the C state and minor effects for the levels of the A state, but robustness of the global envelope behaviour and therefore of the comparison between bound-bound and bound-free contributions which is the main goal of the present contribution.

Figure 2 presents the transition dipole moment from the X$^1\Sigma^+$ ground state to the excited states. We observe
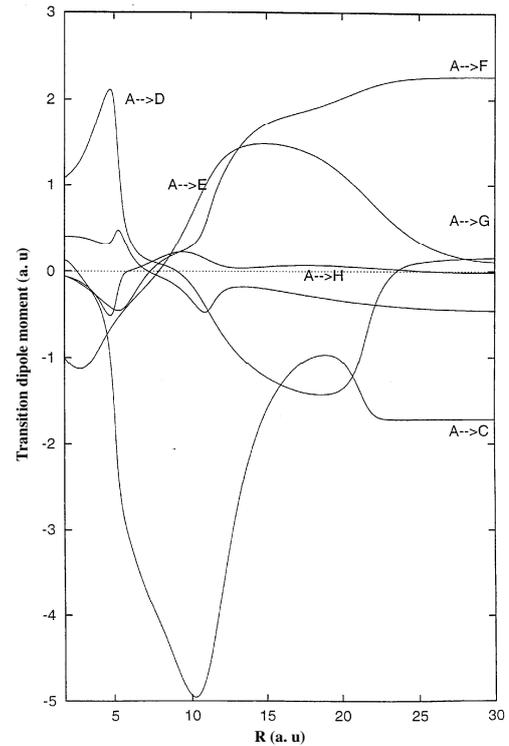
Table 1. X-A$^1\Sigma^+$ Transition dipole moment (in a.u.).

R (a.u)	Our work	Reference [1]	Reference [31]
2.0	.6289	.5895	.6247
2.25	.7019	.6726	.7034
2.50	.7803	.7588	.7855
2.75	.8634	.8474	.8714
3.0	.9510	.9376	.9599
3.25	1.0437	1.0344	1.0503
3.50	1.1425	1.1357	1.1516
3.75	1.2488	1.2443	
4.0	1.3642	1.3624	1.3739
4.50	1.6292	1.6334	1.6223
5.0	1.9467	1.9579	1.9448
5.50	2.3119	2.3299	2.3100
6.0	2.6887	2.7096	2.6956
6.50	2.9963	3.0114	3.0202
7.0	3.1404	3.1419	
7.50	3.0954	3.0809	3.1453
8.0	2.9292	2.9012	
8.5	2.7323	2.6946	2.7686
9.0	2.5626	2.5182	
9.5	2.4437	2.3280	
11.0	2.3505	2.3104	
12.0	2.3616	2.3329	2.3493
15.0	2.3598	2.3436	
20.0	2.3554	2.3449	

Fig. 3. Transition dipole moments from the A$^1\Sigma^+$ to the higher $^1\Sigma^+$ states.

that the most important transition is from the ground state to the first excited state A$^1\Sigma^+$, which has a maximum of 3.14 a.u at a distance $R = 7$ a.u. In fact, only the transition X$^1\Sigma^+$-A$^1\Sigma^+$ has been studied in the past. The values of such transition dipole moment are also presented in Table 1 and compared, in details, with the available works [1,31]. The difference between our values and those of references [1,31] does not exceed 2×10^{-2} a.u. At the asymptotic limit, as it's expected, we found a constant of 2.353 a.u related to the pure atomic transition Li(2s)-Li(2p). This theoretical value is in excellent agreement with the experimental one of 2.3 a.u. Figure 3 is devoted to the transition dipole moment between the A $^1\Sigma^+$ state and the higher excited states. As we can see, the most significant one is associated to the A$^1\Sigma^+$-C$^1\Sigma^+$ transition with a maximum, in absolute value, of about 4.9 a.u, and which reaches, at the asymptotic limit, a constant corresponding to the Li(2p)-Li(3s) pure atomic transition. The other higher transitions from the ground or the first excited states (X $^1\Sigma^+$ and A$^1\Sigma^+$) to higher ones will not be described here as they are presented in Figures 2 and 3.

3.2 Einstein A coefficients and radiative lifetimes

In Table 2, we report the Einstein coefficients and the radiative lifetimes associated to the A$^1\Sigma^+$-X$^1\Sigma^+$ emissions. We present in column 2 the A Einstein coefficients

of the bound-bound contribution associated to the vibrational levels trapped by A$^1\Sigma^+$ electronic state. Columns 3 and 4 are devoted to the bound-free contribution using the Franck-Condon approximation (column 3) proposed by Zemke et al. [36] and by exact calculation (column 4). Columns 5 and 6 correspond to the total approximated and exact lifetimes. We remark, for the first 8 levels, that the bound-free contribution is negligible, which is in good agreement with the results of Zemke et al. [35] and Partridge et al. [1]. For the higher excited vibrational levels the bound-free contribution becomes more important and it is more competitive with the bound-bound transition contribution and in some cases more significant than the latter. For better understanding of the different contributions in the total radiative lifetimes, we have presented in Figure 4 a comparison of our bound-bound contribution with that of Zemke et al. [35] and Partridge et al. [1]. We remark that there is a good agreement between the three works. In Figure 5, we have presented the bound-free contribution where our values were computed by using the Franck-Condon approximation (FC) and exactly. The two calculations are compared also with the works of Zemke et al. [35] and Partridge et al. [1] done using the Frank-Condon approximation. For the lower vibrational levels, there is a good agreement between the four studies; while for the higher levels the exact calculation of the bound-free contribution differs from the Franck-Condon calculation and moreover prevails. The absence of experimental data does not allow deeper comparisons for the higher vibrational levels.

Table 2. Emission rates and radiative lifetime of the vibrational levels trapped in the A $^1\Sigma^+$ state.

Level V	bound-bound ($\times 10^6$ s^{-1})	Bound-free FC ($\times 10^6$ s^{-1})	Bound-free Exact ($\times 10^6$ s^{-1})	Total FC (ns)	Total exact (ns)
0	33.8167	0.0000	0.0000	29.5711	29.5711
1	32.7190	0.0000	0.0000	30.5633	30.5633
2	31.6441	0.0000	0.0000	31.3833	31.3833
3	31.1598	0.0000	0.0000	32.0926	32.0926
4	30.5570	0.0003	0.0001	32.7254	32.7256
5	30.0067	0.0025	0.0008	33.3231	33.3250
6	29.5064	0.0073	0.0026	33.8826	33.8879
7	29.0054	0.0530	0.0224	34.4126	34.4497
8	28.2657	0.3384	0.1625	34.9600	35.1763
9	27.5061	0.6952	0.3728	35.4594	35.8695
10	26.2150	1.6400	0.9797	35.9001	36.7719
11	22.2742	5.0163	3.4907	36.6427	38.8125
12	20.3899	6.7564	5.1644	36.8374	39.1323
13	18.8892	8.2658	6.9716	36.8257	38.6686
14	18.2235	9.1394	8.2840	36.5458	37.7251
15	18.1633	9.5541	9.4032	36.0785	36.2760
16	16.3101	11.8157	12.5926	35.5546	34.5989
17	14.2793	14.3263	16.3664	34.9582	32.6310
18	14.2947	15.0630	18.4190	34.0626	30.5682
19	12.9332	17.3285	22.4110	33.0450	28.2931
20	11.9956	19.2921	26.0665	31.9614	26.2729
21	11.7095	20.7864	29.1849	30.7731	24.4533
22	11.2554	22.5573	32.9075	29.5746	22.6434
23	10.8967	24.2820	36.9582	28.4263	20.8965
24	11.1110	25.2507	40.6978	27.5015	19.3017
25	11.4995	25.6891	45.2758	26.8900	17.6133
26	8.8891	28.3752	55.4741	26.8353	15.5368
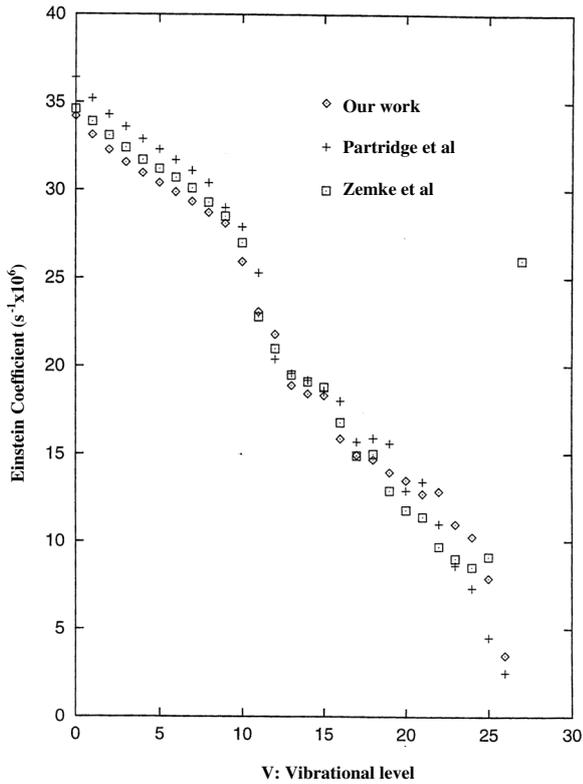
Fig. 4. Bound-bound transition contribution for the A-X$^1\Sigma^+$ transitions.
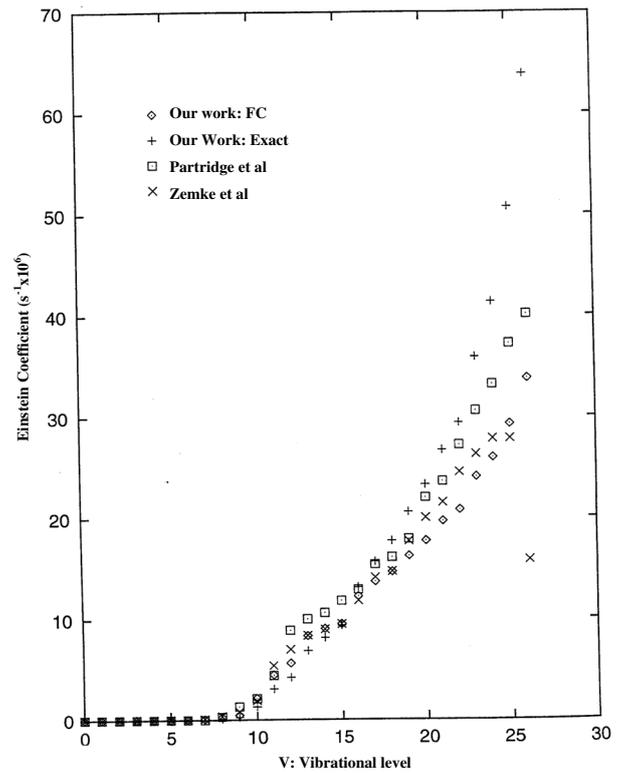
Fig. 5. Bound-free transition contribution to the A-X$^1\Sigma^+$ transitions.

Table 3. Comparison of calculated and experimental radiative lifetimes of the vibrational levels trapped in the A $^1\Sigma^+$ state of LiH.

Level V	This work (FC)	This work (Exact)	Reference [1]	Reference [35]	Reference [34]	Exptl.
0	29.57	29.57	24.3	27.4	28.9	
1	30.56	30.56	24.0	28.4	29.5	
2	31.38	31.38	24.1	29.2	30.2	$29.4 \pm 1.3\,(j=3)^a$
3	32.09	32.09	23.2	29.8	30.8	
4	32.72	32.72		30.4	31.5	
5	33.32	33.32		31.0	32.0	$30.5 \pm 1.3\,(j=3)^a$
						$33.0 \pm 3.5\,(j=0)^b$
						$32.6 \pm 3.0\,(j=5)^b$
						$32.6 \pm 3.0\,(j=10)^b$
						$29.0 \pm 3.2\,(j=15)^b$
6	33.88	33.89		31.6	32.6	
7	34.41	34.45		32.1	33.1	$36.9 \pm 1.9\,(j=12)^a$
8	34.96	35.18		32.6	33.6	$32.2 \pm 5.9\,(j=15)^b$
9	35.46	35.87		33.0	34.2	
10	35.90	36.77		33.3	34.6	
11	36.64	38.81		33.7	35.5	
12	38.84	39.13		34.0	35.7	
13	36.82	38.67		33.8	35.8	
14	36.54	37.72		33.6	35.6	
15	36.08	36.28		32.9	35.4	
16	35.55	34.60		32.3	34.9	
17	34.96	32.63		32.1	34.5	
18	34.06	30.57		31.1	33.7	
19	33.04	28.29		29.9	32.6	
20	31.96	26.27		28.7	31.5	
21	30.77	24.45		27.1	30.4	
22	29.57	22.64		26.2	29.3	
23	28.43	20.90		25.6	28.3	
24	27.50	19.30		24.7	27.5	
25	26.89	17.63		24.0	27.1	
26	26.83	15.54		23.5	27.1	

^{a} Reference [37]. ^{b} Reference [38].

Our exact calculation shows that such approximation is not valid to evaluate the bound-free contribution to the total radiative lifetime for the higher excited levels. In fact, the increase of that contribution will reduce significantly the total radiative lifetime as it's shown in Table 2, where the total radiative lifetimes computed exactly and using the Franck-Condon approximation are reported. In Table 3 we compare our radiative lifetimes with the theoretical works [1,34,35] for all vibrational levels of the A $^1\Sigma^+$ state. However, the comparison with the experimental works [37,38] is done (in the same table) for only a few vibrational levels. Our radiative lifetimes for the A $^1\Sigma^+$ state of the LiH molecule, agree very well with the previous theoretical [1,34,35] and experimental [37,38] ones. For example, the radiative lifetime of the level $v = 5$ (33.25 ns) is in excellent agreement with the experimental [38] value of 33.0 ± 3.5 ns. It's important to note that such excellent agreement was obtained by including the bound-free transition neglected in the past. Our radiative lifetime without the bound-free contribution for such level is 30 ns. The effect of such bound-free contribution is clearly more significant for the higher vibrational levels.

To make profit from the very accurate transition dipole moment, we have performed a similar calculation for the second excited state $C^1\Sigma^+$. However, for this state the total lifetime for a vibrational level trapped by the state $C^1\Sigma^+$ results now from two contributions: the first is associated to the C-A$^1\Sigma^+$ transition and the second to the C-X$^1\Sigma^+$ transition. The $C^1\Sigma^+$-B$^1\Pi$ transitions are not taken into account for the total lifetime in this work. Therefore, the total radiative lifetimes for the vibrational levels of the $C^1\Sigma^+$ state are considered as approximate values for a first evaluation. We present in Table 4 the emission rates and the radiative lifetimes associated to the C-A$^1\Sigma^+$ emissions. The Einstein coefficients related to the bound-bound and bound-free transitions are reported in the three first columns; while the two last columns present the total radiative lifetimes, which are different by the bound-free contribution calculated in the first case by the Franck-Condon approximation and in the second case by exact integration. Table 5 reports the emission rates and the radiative lifetimes associated to the C-X$^1\Sigma^+$ emission. We notice that the lifetime associated to C-A$^1\Sigma^+$ emission is maximum for the level $v = 33$ (190.96 ns), whereas

Table 4. Emission rates of the vibrational levels trapped by the C $^1\Sigma^+$ state: C-A $^1\Sigma^+$ contribution.

V	bound-bound ($\times 10^6$ s^{-1})	Bound-free FC ($\times 10^6$ s^{-1})	Bound-free Exact ($\times 10^6$ s^{-1})
0	10.0584	0.0005	0.0002
1	11.2130	0.0062	0.0031
2	12.3136	0.0306	0.0183
3	13.1382	0.2254	0.1638
4	13.6168	0.5584	0.4821
5	14.0747	0.9077	0.9045
6	13.8025	1.5723	1.8613
7	14.6367	1.6279	2.2479
8	15.6112	1.5268	2.4266
9	15.9944	1.6701	3.0634
10	16.5659	1.7148	3.4383
11	17.1254	1.6860	3.9171
12	176615	1.6565	4.3287
13	18.1655	1.6463	4.7573
14	18.4427	1.6668	5.3163
15	18.8937	1.6080	5.6700
16	19.2187	1.6114	6.2138
17	19.4543	1.6224	6.7812
18	19.8064	1.5656	7.0971
19	19.8444	1.6102	7.8753
20	20.1581	1.5914	8.3116
21	20.4630	1.5630	8.6531
22	20.3671	1.6187	9.4779
23	20.6105	1.5923	9.8197
24	20.7464	1.6162	10.3941
25	20.8616	1.6467	10.9373
26	21.0517	1.6470	11.2296
27	20.9386	1.7248	11.9858
28	21.1351	1.7584	12.3166
29	21,3130	1.8259	12.7062
30	21.3829	1.9293	13.1595
31	21.5642	2.0164	13.3018
32	21.5405	2.1459	13.2186
33	5.1557	0.1536	0.0810
34	20.1328	2.3031	12.8273
35	21.0425	2.5585	12.8516
36	19.4995	2.6137	10.4013
37	14.1582	2.4370	7.0218
38	12.9476	3.3338	9.6997
39	13.9842	4.6592	12.7143
40	13.4208	6.0817	13.6666
41	11.2812	7.7364	14.4593
42	6.3248	9.5120	17.0337

Table 5. Emission rates of the vibrational levels trapped in the C $^1\Sigma^+$ state: C-X $^1\Sigma^+$ contribution

V	bound-bound ($\times 10^6$ s^{-1})	Bound-free FC ($\times 10^6$ s^{-1})	Bound-free Exact ($\times 10^6$ s^{-1})
0	4.4163	2.1325	6.2674
1	2.4683	2.2625	9.2121
2	1.4999	1.7938	9.7469
3	1.3137	1.1968	8.5609
4	0.8126	0.9469	8.8110
5	0.7023	0.6631	7.9276
6	0.5492	0.4769	7.3179
7	0.3243	0.3679	7.2638
8	0.2218	0.2609	6.6394
9	0.0829	0.2061	6.7981
10	0.0549	0.1490	6.3809
11	0.0460	0.1125	6.3169
12	0.0769	0.0835	6.2093
13	0.1442	0.0609	6.0478
14	0.2382	0.0464	6.2238
15	0.3705	0.0333	6.1181
16	0.5318	0.0248	6.3426
17	0.7211	0.0176	6.3263
18	0.9376	0.0125	6.4506
19	1.1787	0.0088	6.5655
20	1.4429	0.0061	6.6320
21	1.7281	0.0042	6.8741
22	2.0297	0.0028	6.9492
23	2.3504	0.0018	7.2073
24	2.6902	0.0010	7.3032
25	3.0540	0.0005	7.4764
26	3.4411	0.0002	7.6117
27	3.8498	0.0001	7.7172
28	4.2793	0.0000	7.9138
29	4.7360	0.0000	8.0076
30	5.2413	0.0001	8.2054
31	5.8529	0.0002	8.2712
32	6.9945	0.0002	8.1868
33	22.8495	0.0000	0.3159
34	7.5280	0.0003	7.7706
35	8.5805	0.0004	7.9134
36	11.1077	0.0004	6.8709
37	12.7089	0.0004	4.8637
38	9.3873	0.0004	5.4317
39	7.9110	0.0004	6.3645
40	7.5705	0.0003	6.3096
41	6.6797	0.0001	5.6378
42	3.9996	0.0001	3.6405

it is minimal for the same level but for the C-X$^1\Sigma^+$ emission (43.16 ns). This phenomenon observed for the level $v = 33$ can be explained by the feature of the wave function of this vibrational level as it belongs to a double well characterizing the C$^1\Sigma^+$ State. The wave function is more significant for the short distances corresponding to the small internal well.

Concerning the contribution of the bound-free transition in the total lifetimes associated to the vibrational levels of the C$^1\Sigma^+$ electronic state, the calculation using the FC approximation is often in disagreement with the exact calculation especially in the case of the C-A$^1\Sigma^+$

emission. This shows the limitation of the approximation suggested by Zemke et al. [35]. The use of the transition dipole moment at the external turning point is not reasonable any more. The total lifetimes of the vibrational levels of the C$^1\Sigma^+$ state by carrying out an approximate or exact calculation of the bound-free contribution and considering the C-X$^1\Sigma^+$ and C-A$^1\Sigma^+$ emissions are gathered in Table 6. We observe that the lifetimes associated to the C-A$^1\Sigma^+$ emission generally dominate that associated to the C-X$^1\Sigma^+$ emission as can be expected since the energy difference is smaller. The radiative lifetimes of the vibrational levels of the C$^1\Sigma^+$ state are generally of the same

Table 6. Total approximated Frank-Condon (FC) and exact radiative lifetimes of the vibrational levels trapped in the C $^1\Sigma^+$ state.

Level V	FC (ns)	Exact (ns)
0	60.21	48.21
1	62.70	43.67
2	63.95	42.41
3	63.00	43.15
4	62.75	42.15
5	61.17	42.35
6	60.97	42.49
7	58.97	40.86
8	56.75	40.16
9	55.70	38.55
10	54.10	37.68
11	52.71	36.49
12	51.34	35.36
13	49.96	34.34
14	49.03	33.09
15	47.83	32.20
16	46.76	30.95
17	45.84	30.04
18	44.80	29.16
19	44.16	28.19
20	43.11	27.36
21	42.09	26.51
22	41.63	25.76
23	40.72	25.01
24	39.91	24.31
25	39.11	23.62
26	38.25	23.07
27	37.72	22.47
28	36.80	21.91
29	35.87	21.38
30	35.02	20.84
31	33.97	20.41
32	32.59	20.02
33	35.51	35.21
34	33.37	20.72
35	31.07	19.85
36	30.10	20.88
37	34.12	25.80
38	38.95	26.69
39	37.66	24.41
40	36.94	24.41
41	38.78	26.21
42	50.41	32.26

order of magnitude as those of $A^1\Sigma^+$ state. The first levels have radiative lifetimes of about 40 ns. This is also the case for the level 33, belonging simultaneously to the two wells characterizing the electronic state C $^1\Sigma^+$. There are neither theoretical nor experimental results concerning the radiative lifetimes of the vibrational levels of the C state. The results presented here for the C$^1\Sigma^+$ state can constitute the first predictions. It is important to note that Tables 2–6 comprise all the bound vibrational levels of the A and C states.

4 Conclusion

In this paper, we have presented the transition dipole moment of the LiH molecule from the $X^1\Sigma^+$ and $A^1\Sigma^+$ states to the higher excited states of the same symmetry. The comparison of the X-A$^1\Sigma^+$ transitions with the available theoretical works [1,31], has shown the high accuracy of our transition dipole moment. Such transition moments were used to determine the radiative lifetimes for all the vibrational levels trapped in the A and C $^1\Sigma^+$ excited states of the LiH molecule. We have used in this calculation very accurate potential energy curves determined previously [10]. The good agreement of the spectroscopic constants with the theoretical and experimental data has shown the efficiency of such ab initio data. Our radiative lifetimes for the vibrational levels of the A $^1\Sigma^+$ state of the LiH molecule agree very well with the available data [1,34,35,37,38]. In addition, we have evaluated, for the first time, the radiative lifetimes of all vibartional levels of the C $^1\Sigma^+$ state. Although, the C$^1\Sigma^+$-B$^1\Pi$ emission contribution was not considered, the performed values can be considered as a first prediction of the lifetimes for the second excited state, C$^1\Sigma^+$. The bound-free contribution is calculated exactly and using the Franck-Condon approximation. Such term was included in the total radiative lifetime, together with the bound-bound term, and a significant change in the total radiative lifetimes has been observed, particularly for the higher excited vibrational levels, where the approximate evaluation breaks down. The present work clearly shows that the bound free contribution to the radiative lifetime cannot be neglected for the A and C states of LiH particularly foe the higher excited levels, as it was also the case for C state of H_2 [45,46]. This conclusion is expected to be of broad generality.

References

1. H. Partridge, R.S. Langhoff, J. Chem. Phys. **74**, 2361 (1981)
2. K.K. Docken, J. Hinze, J. Chem. Phys. **57**, 4928 (1972)
3. K. Sasagane, K. Mori, A. Ichihara, R. Itoh, J. Chem. Phys. **92**, 3619 (1990)
4. X.C. Wang, K.F. Freed, J. Chem. Phys. **91**, 32 (1989)
5. S. Ben-Shlomo, U. Kaldor, J. Chem. Phys. **89**, 956 (1988)
6. L. Mendez, I.L. Copper, A.S. Dickinson, O. Mo, A. Riera, J. Phys. B **23**, 2797 (1990)
7. A. Balkova, S.A. Kucharski, L. Meissner, P.J. Bartlett, J. Chem. Phys. **95**, 4311 (1991)
8. K.R. Way, W.C. Stawlly, J. Chem. Phys. **59**, 5298 (1973)
9. Y.C. Chan, D.R. Hardingand, W.C. Stwalley, C.V. Vidal, J. Chem. Phys. **85**, 2436 (1986)
10. A. Boutalib, F.X. Gadéa, J. Chem. Phys. **97**, 1144 (1992)
11. H. Berriche, F.X. Gadéa, Chem. Phys. Lett. **247**, 85 (1995)
12. F.X. Gadéa, H. Berriche, O. Romero, P. Villarreal, G.D. Barrio, J. Chem. Phys. **107**, 10515 (1997)
13. F.X. Gadéa, F. Gemperle, H. Berriche, P. Villareal, G.D. Barrio, J. Phys. B **30**, 427 (1997)
14. W. Zrafi, B. Oujia, H. Berriche, F.X. Gadéa, J. Mol. Struct. **777**, 87 (2006)

15. F. Gemperle, F.X. Gadéa, J. Chem. Phys. **110**, 11197 (1999)
16. F.A. Gianturco, P. Gori Giorgi, H. Berriche, F.X. Gadéa, Astron. Astrophys. Suppl. Ser. **117**, 377 (1996)
17. K.K. Docken, J. Hinze, J. Chem. Phys. **57**, 4936 (1972)
18. C.F. Bender, E.R. Davidson, J. Chem. Phys. **49**, 4222 (1968)
19. H. Partridge, S.R. Langhoff, W.C. Stwalley, W.T. Zemke, J. Chem. Phys. **75**, 2299 (1981)
20. D.M. Bishop, L.M. Cheung, J. Chem. Phys. **78**, 1396 (1983)
21. D.M. Bishop, L.M. Cheung, J. Chem. Phys. **78**, 7265 (1983)
22. D.M. Bishop, L.M. Cheung, J. Chem. Phys. **41**, 3663 (1964)
23. J.O. Jensen, D.R. Yarkony, J. Chem. Phys. **89**, 975 (1988)
24. C.R. Vidal, W.C. Stwalley, J. Chem. Phys. **77**, 883 (1982)
25. Y.C. Chan, D.R. Harding, W.C. Stwalley, C.R. Vidal, J. Chem. Phys. **85**, 2437 (1986)
26. N. Geum, G.H. Jeung, A. Derevianko, R. Côté, A. Dalgarno, J. Chem. Phys. **115**, 5984 (2001)
27. K.K. Docken, J. Hinze, J. Chem. Phys. **73**, 4936 (1972)
28. L. Wharton, L.P. Gold, W. Klemper, J. Chem. Phys. **33**, 1255 (1960)
29. L. Wharton, L.P. Gold, W. Klemper, J. Chem. Phys. **37**, 2149 (1962)
30. E. Rothstein, J. Chem. Phys. **50**, 1899 (1969)
31. H. Partridge, S.R. Langhoff, W.C. Stwalley, W.T. Zemke, J. Chem. Phys. **75**, 2299 (1981)
32. K.K. Docken, J. Hinze, J. Chem. Phys. **57**, 4928 (1972)
33. M. Brieger, A. Renn, A. Sodeik, Chem. Phys. Lett. **76**, 465 (1980)
34. P.J. Dagdigian, J. Chem. Phys. **73**, 2049 (1980)
35. W.T. Zemke, J.B. Crooks, W.C. Stwalley, J. Chem. Phys. **68**, 4628 (1978)
36. S.J. Till, S.T. Howard, I.W. Parsons, J. Chem. Phys. **95**, 9079 (1991)
37. P.J.Dagdigian, J. Chem. Phys. **64**, 2609 (1976)
38. P.H. Wine, L.A. Melton, J. Chem. **64**, 2692 (1976)
39. S.K. Tokunaga, J.O. Stack, J.J. Hudson, B.E. Sauer, E.A. Hinds, M.R. Tarbutt, J. Chem. Phys. **126**, 124314 (2007)
40. N. Bouloufa, L. Cabaret, P. Luc, R. Vetter, W.T. Luh, J. Chem. Phys. **121**, 7237 (2004)
41. F.X. Gadéa, M. Pellissier, J. Chem. Phys. **93**, 545 (1990)
42. W.C. Tung, L. Adamowicz, J. Chem. Phys. **140**, 124315 (2014)
43. F.X. Gadéa, T. Leininger, Teor. Chem. Acc. **116**, 566 (2006)
44. T.L. Stephens, A. Dalgarno, J. Quant. Spectrosc. Radiat. Transfer **12**, 569 (1972)
45. A. Pardo, Spectrochim. Acta **54**, 1433 (1998)
46. A. Pardo, J. Mol. Spectrosc. **195**, 68 (1999)
47. Y.L. Huang, W.T. Luh, G.H. Jeung, F.X. Gadéa, J. Chem. Phys. **113**, 683 (2000)
48. C.Y. Wu, W.T. Luth, F.X. Gadéa, W.C. Stwalley, J. Chem. Phys. **128**, 064303 (2008)
49. F. Gemperle, F.X. Gadéa, Europhys. Lett. **48**, 513 (1999)