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Radiative lifetimes for the A $^1\Sigma^+$ state of the KH molecule

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Abstract. The spontaneous radiative lifetime of rovibrational levels of the KH A $^1\Sigma^+$ state for $v' = 0$–39 and $J' = 1, 15, 30, 45$ and 60 are calculated. Rydberg–Klein–Rees (RKR) electronic potentials for the A $^1\Sigma^+$ and X $^1\Sigma^+$ states are utilized. Bound–bound and bound–free Einstein emission coefficients are calculated for rovibrational levels in order to obtain radiative lifetimes. A comparison with experimental measured lifetimes is presented.

(Some figures in this article are in colour only in the electronic version; see www.iop.org)

1. Introduction

The study of radiative lifetimes of diatomic molecules is of great interest from the experimental and theoretical point of view. There are few related experimental or theoretical works on the subject. The lifetimes of the A $^1\Sigma^+$ state of the KH molecule have been studied experimentally for $v' = 5, 7, 10, 13, 17, 18$ and 22, and some J' levels (lower than 10) [1]. One important aspect is the appearance in the fluorescence spectra of the bound–free (BF) transitions that accompany the bound–bound (BB) emission. To calculate lifetimes the bound–free transitions must be taken into account.

Bound–free emission for the hydrogen molecule has been discussed by Stephens and Dalgarno (SD) [2]. The calculation of the radiative lifetimes for the B $^1\Sigma_u^+$ and C $^1\Pi_u$ H$_2$ states, bearing in mind the effect of the bound–free transitions, has been shown in recent works [3]. In the LiH A $^1\Sigma^+$ state the lifetimes have been calculated for all the v' [4, 5]. In the work of Stephens and Dalgarno, a detailed consideration of the theory associated with the bound–bound and bound–free transitions is presented in order to calculate the radiative lifetimes and continuum emission spectra.

In this letter, the principal objective is the study of the rotational effect on the lifetimes for the A $^1\Sigma^+$ KH state and the contribution of bound–free transitions, in order to make a comparison with experimental values. We show the results of A $^1\Sigma^+$–X $^1\Sigma^+$ emission of KH molecules for $v' = 0$–39 and $J' = 1, 15, 30, 45$ and 60 and the comparison with experimental measured lifetimes. We considered $J' = 1$ and not $J' = 0$, only to standardize the calculations: for $J' = 0\,(\Delta J = -1)$, but for $J' = 1$, $\Delta J = \pm 1$ and for $J' = 15, 30, 45$ and 60, $\Delta J = \pm 1$.
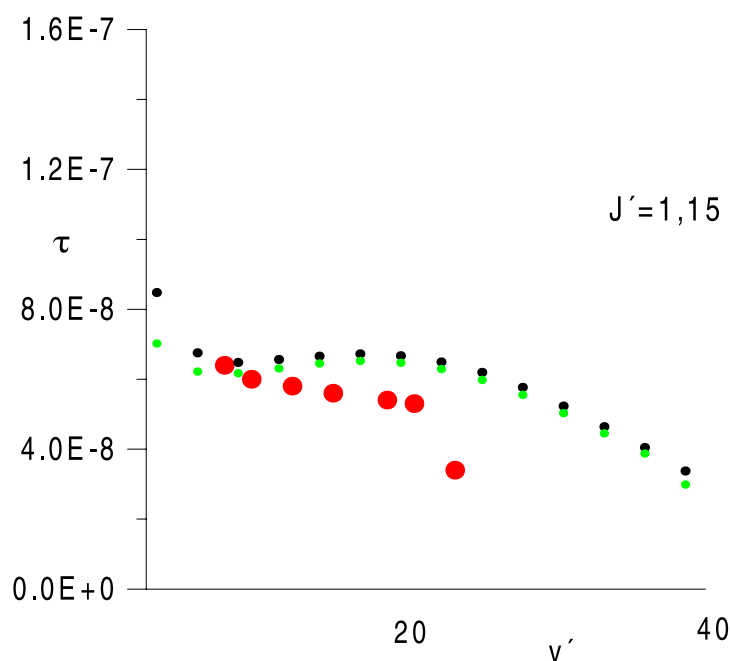
Figure 1. Comparison of the calculated lifetimes for $J' = 1, 15$ (obtained with the dipole transition moment presented in [6]) and the experimental lifetimes (from [1]) for the A $^1\Sigma^+$–X $^1\Sigma^+$ transition of KH molecules.

Table 1. Values for the dipole transition moment for A $^1\Sigma^+$–X $^1\Sigma^+$ transition of KH molecules (Debye and Angström units).

r	D	r	D	r	D	r	D
1.32	4.46	2.53	4.02	3.75	6.95	6.19	6.52
1.55	4.31	2.77	4.26	4.24	8.28	6.68	6.32
1.80	4.14	3.02	4.70	4.72	8.21	7.16	6.25
2.04	4.01	3.26	5.30	5.21	7.48	7.65	6.34
2.29	3.95	3.51	6.05	5.70	6.89	8.63	6.69
						10.58	7.44

2. Calculations

RKR potentials obtained in previous work, for A $^1\Sigma^+$ and X $^1\Sigma^+$ KH states [6], have been used to calculate bound–bound and bound–free radiative transition probabilities. These potentials were obtained from the information for the KH, A $^1\Sigma^+$ and X $^1\Sigma^+$ electronic states. Using the spectroscopic constants reported by Stwalley *et al* [7] for the ground state of KH, we determined the RKR points for the X $^1\Sigma^+$ state. Likewise, from the spectroscopic constants reported by Rafi *et al* [8] for the A $^1\Sigma^+$ state of KH, obtained from the data of Bartky [9] and Rafi *et al* [10], we determined the RKR potential for the A $^1\Sigma^+$ state.

In order to calculate radiative transition probabilities, it is necessary to know the transition dipole moment function. For KH, there is no *ab initio* quantum mechanical calculation of the A $^1\Sigma^+$–X $^1\Sigma^+$ transition dipole moment function. To calculate this function we used the following procedure. From the experimental lifetimes of the upper A $^1\Sigma^+$ vibrational levels

Table 2. Radiative lifetimes (τ in seconds) for $v' = 0$–39 and $J' = 1, 15, 30, 45, 60$ of the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition of KH molecules.

	J'				
v'	1	15	30	45	60
0	7.47E−08	8.08E−08	9.62E−08	1.18E−07	1.42E−07
1	7.10E−08	7.66E−08	9.07E−08	1.10E−07	1.31E−07
2	6.77E−08	7.27E−08	8.60E−08	1.04E−07	1.23E−07
3	6.52E−08	6.97E−08	8.22E−08	9.97E−08	1.18E−07
4	6.33E−08	6.75E−08	7.90E−08	9.58E−08	1.13E−07
5	6.17E−08	6.56E−08	7.65E−08	9.24E−08	1.08E−07
6	6.05E−08	6.41E−08	7.45E−08	8.93E−08	1.04E−07
7	5.94E−08	6.29E−08	7.27E−08	8.67E−08	9.99E−08
8	5.87E−08	6.19E−08	7.10E−08	8.42E−08	9.62E−08
9	5.83E−08	6.10E−08	6.96E−08	8.20E−08	9.27E−08
10	5.77E−08	6.03E−08	6.82E−08	7.99E−08	8.93E−08
11	5.73E−08	5.97E−08	6.71E−08	7.79E−08	8.60E−08
12	5.70E−08	5.91E−08	6.60E−08	7.60E−08	8.29E−08
13	5.66E−08	5.87E−08	6.49E−08	7.41E−08	7.98E−08
14	5.64E−08	5.83E−08	6.40E−08	7.22E−08	7.68E−08
15	5.63E−08	5.79E−08	6.30E−08	7.04E−08	7.38E−08
16	5.60E−08	5.75E−08	6.21E−08	6.86E−08	7.09E−08
17	5.56E−08	5.71E−08	6.12E−08	6.67E−08	6.80E−08
18	5.53E−08	5.66E−08	6.03E−08	6.49E−08	6.52E−08
19	5.50E−08	5.61E−08	5.93E−08	6.31E−08	6.23E−08
20	5.45E−08	5.56E−08	5.83E−08	6.12E−08	5.94E−08
21	5.40E−08	5.50E−08	5.72E−08	5.93E−08	5.66E−08
22	5.35E−08	5.43E−08	5.61E−08	5.74E−08	5.38E−08
23	5.29E−08	5.36E−08	5.50E−08	5.54E−08	5.11E−08
24	5.23E−08	5.28E−08	5.38E−08	5.47E−08	4.84E−08
25	5.16E−08	5.19E−08	5.25E−08	5.40E−08	4.59E−08
26	5.08E−08	5.10E−08	5.11E−08	5.18E−08	4.34E−08
27	4.99E−08	5.00E−08	4.97E−08	4.96E−08	4.08E−08
28	4.90E−08	4.89E−08	4.81E−08	4.74E−08	3.73E−08
29	4.79E−08	4.77E−08	4.66E−08	4.52E−08	
30	4.68E−08	4.64E−08	4.50E−08	4.31E−08	
31	4.56E−08	4.51E−08	4.34E−08	4.09E−08	
32	4.43E−08	4.37E−08	4.17E−08	3.84E−08	
33	4.29E−08	4.23E−08	4.01E−08		
34	4.16E−08	4.08E−08	3.84E−08		
35	4.02E−08	3.94E−08	3.67E−08		
36	3.87E−08	3.79E−08	3.43E−08		
37	3.73E−08	3.63E−08			
38	3.57E−08	3.43E−08			
39	3.36E−08				

reported by Giroud and Nedelec we obtained an electronic transition dipole moment function with the r-centroid approximation. These calculations and additional considerations have been presented in previous work [6]. Using this transition dipole moment function we now proceed to calculate the lifetimes for the $A\,^1\Sigma^+$ state. The calculated lifetime values show a great discrepancy with the corresponding experimental values, see figure 1. In this figure we show the lifetime calculated values for $v' = 0$–39 ($J' = 1, 15$) and the experimental values reported by Giroud and Nedelec (the large full circles). To correct these discrepancies, the transition

dipole moment has been revised to obtain agreement with the experimental lifetimes obtained by Giroud and Nedelec (see below). These new dipole transition moments are presented in table 1. To obtain this new dipole transition moment function we consider the linear function that was calculated in [6] using the r-centroid approximation. For the intermediate zone of r values this approach is good. However, for large and small r values this approach is inadequate. For these zones, variations were made until we arrived at an appropriate correlation with all the well known experimental lifetimes (for low rotation). In our previous work [6] we considered only an appropriate correlation for the lifetime for $v' = 7$. This can be appreciated from figure 1, where the coincidence (experimental–calculated) for $v' = 7$ is satisfactory. If we compare the two dipole transition moment functions, the most important variations are for low r values (see figure 5). Subsequently, the same numerical integration program was used to obtain eigenvalues and wavefunctions (for all rovibrational studied levels). The information that is introduced is the electronic potential without rotation, the rotational operator, the necessary physics constants and KH reduced mass. With the wavefunctions and new dipole transition moment values, the Einstein emission coefficients (A) are calculated for the rovibrational levels $v' = 0$–39 and $J' = 1, 15, 30, 45$ and 60 (for the A $^1\Sigma^+$–X $^1\Sigma^+$ transition).

   To calculate the lifetime for a rovibrational level in the A $^1\Sigma^+$ state (for the A $^1\Sigma^+$– X $^1\Sigma^+$ transition), $\Delta J = \pm 1$ is considered. The calculated A Einstein emission coefficients (with $\Delta J = \pm 1$) are for all bound–bound transitions. In addition, bound–free transitions are calculated (examples for these are presented in figure 6). In our previous work [6], only $\Delta J = \pm 1$ BB calculated transitions were considered. Our intention to calculate the BF transitions (equation (13) in our previous work was not adequate) did not result in our obtaining appropriate values for comparison with the experimental lifetimes. Additionally, as we have seen [6], the previous transition dipole moment is not suitable (see figure 5). For all of these reasons, the contributions of the BF transitions were considered keeping in mind the experimental lifetimes [1] and the calculated BB transitions in [6]. Now a better approximation can be presented. The conclusions in the work by Stephens and Dalgarno have been applied adequately. The calculation for the bound–free transitions has been performed for some states of the hydrogen molecule, with satisfactory results [3]. With the present calculations and the inverse of the sum $\sum A$ (BB) and $\int A$ (BF) adequate radiative lifetimes are obtained.

$$\tau = 1 \bigg/ \left(\sum A(\text{BB}) + \int A(\text{BF}) \right).$$

The lifetimes (τ) for the studied levels are shown in table 2.

3. Discussion

In figure 2, the $\sum A(\text{BB})$ values are presented as a function of vibration and rotational quantum number. In figure 3, the contribution of $\int A(\text{BF})$ is shown. In figure 4, the radiative lifetimes (τ) are shown. In these three figures, a column with J' values of J' is presented. For example, in figure 2, the $\sum A(\text{BB})$ values for $J' = 1$ ($v' = 0$–39) are presented in the upper part of the figure. Lower down are values corresponding to $J' = 15, 30, 45$ and 60. In figure 3, the $\int A(\text{BF})$ values for $J' = 60$ ($v' = 0$ to the last v' considered) are presented in the upper part of the figure. Lower down are values corresponding to $J' = 45, 30, 15$ and 1. The radiative lifetimes are represented (in figure 4), in the same way as in figure 3 ($J' = 60, 45, 30, 15$ and 1). However, near $v' = 20$ an inflection point appears.

   As is apparent in figure 3, there are significant contributions from bound–free transitions. These contributions are negligible only for low vibrational levels and low rotation. The accumulated effect of $\sum A(\text{BB})$ and $\int A(\text{BF})$ is represented in figure 4 with the radiative
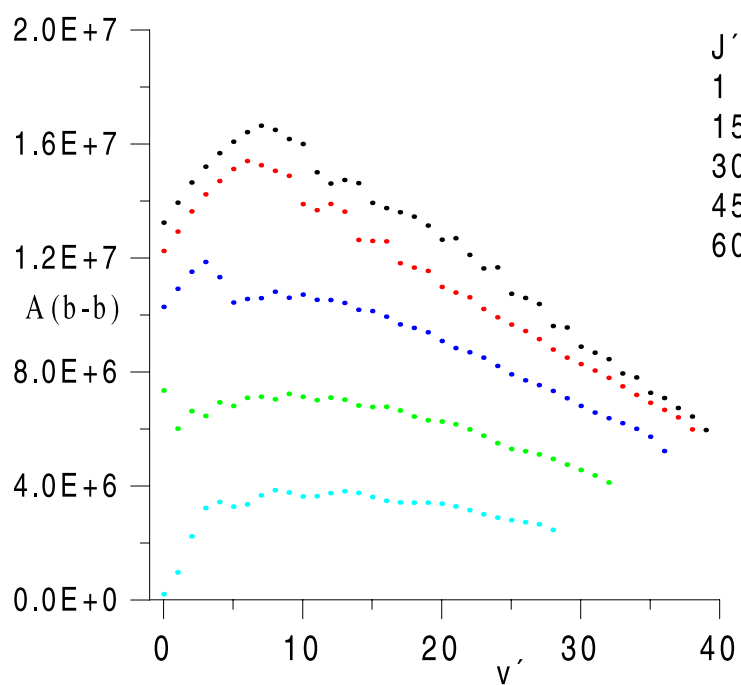
Figure 2. Representation of the sum of bound–bound Einstein A (s^{-1}) coefficients for $v' = 0$–39 and $J' = 1, 15, 30, 45, 60$ of the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition of KH molecules. The order of J' is shown in the figure.
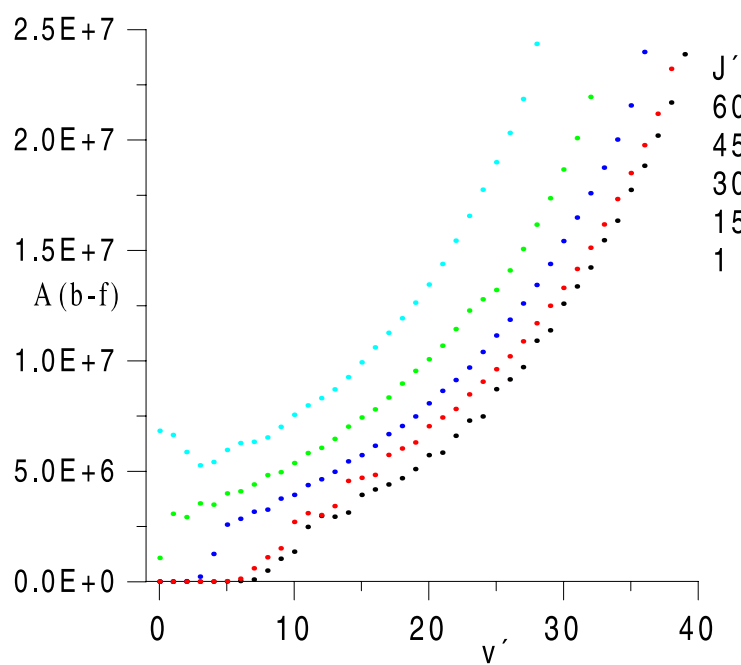
Figure 3. Representation of the integral of bound–free Einstein A (s^{-1}) coefficients for $v' = 0$–39 and $J' = 1, 15, 30, 45, 60$ of the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition of KH molecules. The order of J' is shown in the figure.
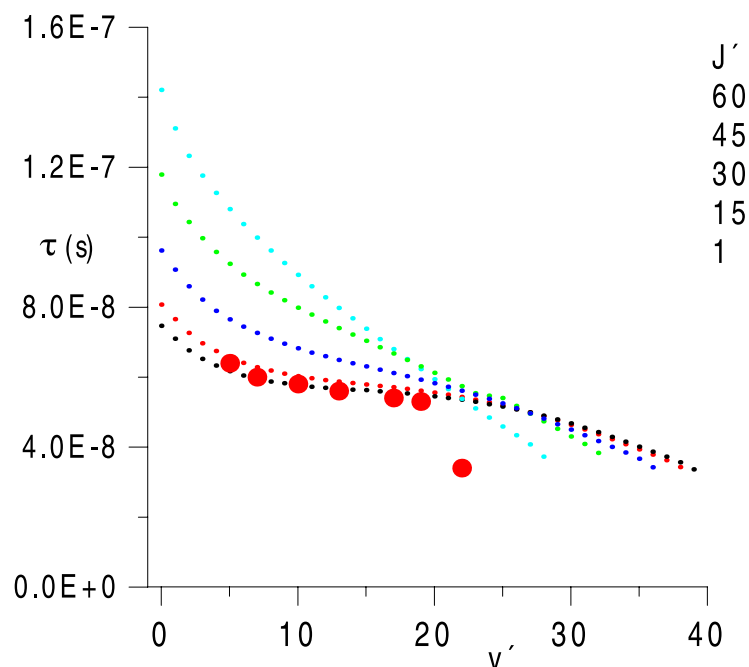
**Figure 4.** Representation of the radiative lifetimes (τ in seconds) for $v' = 0$–39 and $J' = 1, 15, 30, 45, 60$ of the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition of the KH molecule. The order of J' is shown in the figure.

lifetime (τ) for all the rovibrational levels that have been studied. In figure 4 we show (as large full circles) the measured lifetimes by Giroud and Nedelec. These experimental lifetimes are for $A\,^1\Sigma^+$ KH vibrational levels; $v' = 5, 7, 10, 13, 17, 18$ and 22, and some J' levels (lower than 10). We note from figure 4 a good agreement between experimental and calculated lifetimes. Only the experimental lifetime for $v' = 22$ is clearly in disagreement with the corresponding calculated lifetime. In the work by Giroud and Nedelec the discontinuity for this lifetime is attributed to perturbation of $A\,^1\Sigma^+$ at high v' by the dissociative $a\,^3\Sigma$ state. Here we have not considered this perturbation. In figure 4, we can note that the lifetime decreases with v'. For low v', the lifetime increases with rotation, but for the last vibrational levels there is an inversion of this pattern of behaviour. For vibrational levels with high v' consideration of additional perturbations must be taken into account.

For comparison, in figure 5 the two dipole transition moment functions utilized in the present calculations are represented. A comparison of figures 1 and 4 shows that the new dipole transition moment function explains adequately the experimental lifetimes.

In figure 6, a few examples of spectra for rovibrational levels in the $A\,^1\Sigma^+$ KH state with an appreciable participation of bound–free transitions are shown. The continuous spectra are represented by heavy lines. This figure demonstrates the appropriateness of the procedure we have used to calculate the bound–free (continuum) transitions. For the system ($A\,^1\Sigma^+$–$X\,^1\Sigma^+$ in KH molecules) there is no known experimental evidence of this emission continuum for comparison. The procedure that we have used here to calculate the transitions to the continuum was proven for the hydrogen molecule in [3].
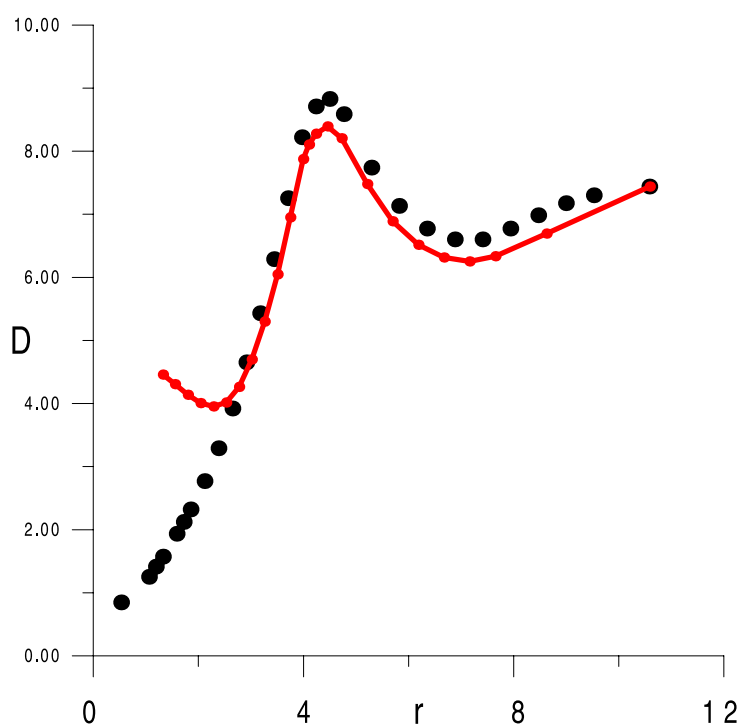
Figure 5. Representation of the dipole transition moment (DTM). Full circles DTM in [6]. Curve with dots, the DTM in this work. Debye and Angström units.
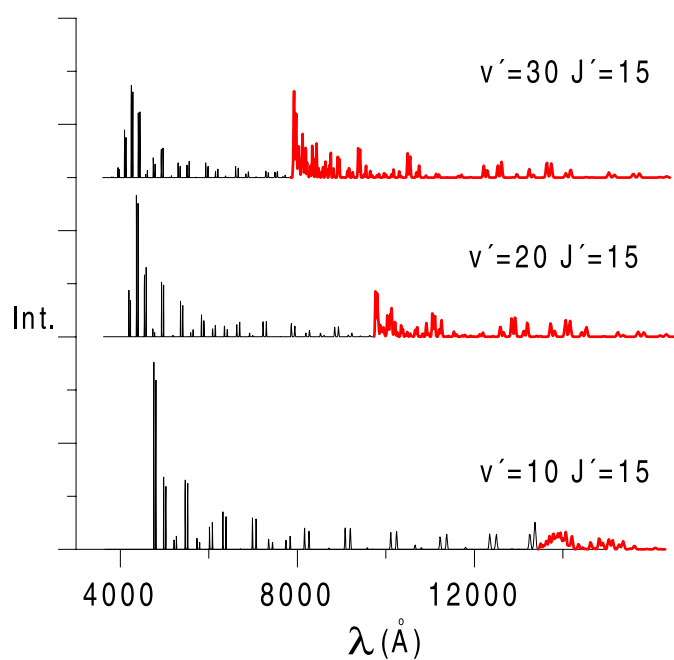
Figure 6. Representation of discrete and continuum spectra for three (indicated in the figure) rovibrational levels of the A $^1\Sigma^+$ KH state. The intensity is in relative units.

4. Conclusions

In this letter, we have introduced rotation and its influence on lifetimes. An effective transition dipole moment function is obtained. The calculation of the lifetimes of the A $^1\Sigma^+$ KH state requires the inclusion of bound–free transitions. The calculated lifetimes are in agreement with experimental lifetimes for low rotation. An appropriate procedure is used in this work to calculate the bound–free transitions. In the procedure used in the previous work [6], spaces of 2 and 20 cm^{-1} were considered in the calculation of continuum wavefunctions. This was inadequate.

Acknowledgments

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