

MOLECULAR SPIN–ORBIT INTERACTION IN THE $A^2\Pi$ STATES OF NaKr AND NaXe*

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The parameter A_D of centrifugal distortion of molecular spin–orbit interaction has been calculated by means of second-order perturbation theory for the $A^2\Pi$ states of NaKr and NaXe using the spin–orbit operator $A(r)$ and the interatomic potential as deduced from high-resolution spectroscopic data. The calculated values of A_D are in reasonable agreement with the experimental results corroborating the validity of $A(r)$. In addition, information on the second-order parameter α_D , being experimentally unobservable in molecular doublet states, has been obtained.

1. Introduction

High-resolution spectroscopic investigations of diatomic molecules are a suitable tool in order to get accurate information on the interatomic potential $V(r)$ in a certain electronic state. The inversion of experimental spectroscopic parameters into $V(r)$ has frequently been performed by the well-known Rydberg–Klein–Rees (RKR) procedure which uses the vibrational energy levels E_v and the rotational constants B_v as input data [1]. Considerable improvements of the inversion procedure have been obtained in recent years, e.g. by using suitable analytical expressions for $V(r)$ with only few parameters. The energy values of the rovibrational levels are deduced from $V(r)$ by means of a quantum-mechanical calculation varying the parameters of $V(r)$ until agreement between calculated and observed term values is achieved in a least-squares sense [2, 3]. This method of approach has successfully been applied recently to the case of the van der Waals molecules NaKr [3] and NaXe [4]. As the input data consist of the observed term values, the effect of the parameters D_v and H_v of centrifugal distortion is automatically included into the inversion procedure.

Much less effort has been devoted to the determination of the spin–orbit operator $A(r)$ from experimental data. $A(r)$ is of relevance for all non-singlet electronic states with $\Lambda > 0$, but we restrict ourselves to the case of $^2\Pi$ states in the following. From the theoretical point of view $A(r)$ can be obtained by means of an ab-initio calculation solving the electronic part of the molecular Schrödinger equation with fixed nuclei including spin–orbit interaction for different values of the internuclear

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separation r . However, reliable calculations of this kind are only available in few exceptional cases. On the other hand, information on $A(r)$ may be deduced from experimentally observed spin-orbit coupling constants A_v as A_v is the vibrational average over $A(r)$ [5]. If experimental data on A_v are available for almost all vibrational levels of an electronic state, a reliable determination of $A(r)$ is possible within the complete range of the bound well.

Molecular spin-orbit splitting is likewise affected by centrifugal distortion of the rotating molecule leading to the additional spectroscopic parameters A_{D_v} and A_{H_v} which are the spin-orbit counterparts of the corresponding rotational parameters D_v and H_v . Experimentally determined values A_{D_v} represent an additional source of information on $A(r)$ which is particularly useful, if only a limited number of vibrational levels is accessible to the experiment. A general procedure for the inversion of A_v and A_{D_v} into $A(r)$ has been developed by Watson [6] using the same semiclassical approach as for the RKR method. However, Watson's approach again requires a knowledge of A_v and A_{D_v} for the complete set of vibrational levels.

In our recent spectroscopic work on the $A^2\Pi$ states of the van der Waals molecules NaKr [3] and NaXe [4] only a restricted set of 7 vibrational levels out of a total of about 30 levels could be observed. The interatomic potentials of the two substates $\Pi_{1/2}$ and $\Pi_{3/2}$ have been determined separately by means of a least-squares fit procedure using suitable analytical expressions as mentioned above. $A(r)$ is obtained as the difference between the two potentials, which are most reliable over the r range covered by the vibrational levels being investigated.

The purpose of the present paper was to calculate the parameter A_{D_v} of the $A^2\Pi$ states of NaKr and NaXe using $A(r)$, to compare the outcome with the experimental result, and to predict values of A_{D_v} for vibrational levels which have not been investigated up to now. There is another second-order parameter a_{D_v} of molecular fine structure depending on $A(r)$ (see the next Section) which leads to a common shift of all rovibrational levels of a molecular doublet state and, therefore, cannot be determined experimentally. However, in order to get an approximate knowledge of its size we have also calculated values of a_{D_v} for the $^2\Pi$ state of NaKr and NaXe.

2. Theory and method of calculation

Before presenting the details of the theoretical treatment, we will give a simple classical picture of the physical origin of the parameter A_D . Considering the molecule as a rigid rotator with internuclear separation r_e , the spin-orbit splitting would be $A(r_e)$ independent of the vibrational and rotational quantum number. Due to centrifugal distortion the molecule, considered as a non-rigid rotator, assumes an equilibrium distance r which by means of classical mechanics is estimated to be $(r - r_e)/r_e \approx \mu J^2/k\Theta_e^2$ (μ reduced mass, J rotational angular momentum, k force constant, Θ_e moment of inertia). In this case, the molecular spin-orbit splitting $A(r)$ includes a small correction term to $A(r_e)$ which is proportional to

$J(J+1)$, the constant of proportionality being A_D . Near equilibrium A_D should be positive, if $A(r)$ increases for $r > r_e$ and vice versa.

For a quantum mechanical treatment of the effect of centrifugal stretching [7-9] the molecular Hamiltonian H for a Hund's coupling case (a) is usually written as

$$H = H_{ev} + A(r)L_zS_z + B(r)(\mathbf{J} - \mathbf{S})^2, \quad (1)$$

where H_{ev} is the electronic and vibrational part. As we restrict ourselves to interactions within a given electronic state, the parts of the spin-orbit operator $A(r)\mathbf{L} \cdot \mathbf{S}$ being non-diagonal with respect to orbital and spin angular momentum \mathbf{L} and \mathbf{S} have been omitted in Eq. (1). The third term on the right hand side of Eq. (1) is the well-known effective operator of molecular rotation as given by Brown et al [10] with $B(r) = \hbar^2/2\mu r^2$ and \mathbf{J} denoting the total angular momentum. Now, we apply standard perturbation theory to Eq. (1) using $H' = A(r)L_zS_z + B(r)(\mathbf{J} - \mathbf{S})^2$ as a perturbation. In zeroth order the eigenvalues and eigenvectors of H_{ev} are the vibrational energies E_v and the wavefunctions $|v\rangle$ of nuclear vibration, respectively. The electronic part is the same for all vibrational levels and may, therefore, be omitted. The first order contribution $E_{vJ}^{(1)}$ to the energy of a rovibrational level of a doublet state with $\Sigma = \pm 1/2$ is given by

$$E_{vJ}^{(1)} = A_v\Lambda\Sigma + B_v \left[J(J+1) + \frac{1}{4} - 2\Lambda\Sigma \right], \quad (2)$$

with $A_v = \langle v|A(r)|v\rangle$ and $B_v = \langle v|B(r)|v\rangle$. For the second-order part $E_{vJ}^{(2)}$ we obtain after some calculation for a doublet state

$$E_{vJ}^{(2)} = -D_v \left\{ [J(J+1)]^2 + \left(\frac{3}{2} - 4\Lambda\Sigma \right) J(J+1) - \Lambda\Sigma + \frac{5}{16} \right\} + A_{D_v}\Lambda\Sigma \left[J(J+1) + \frac{1}{4} - 2\Lambda\Sigma \right] + \frac{1}{4}\Lambda^2 a_{D_v}, \quad (3)$$

introducing three second-order parameters D , A_D and a_D

$$D_v = - \sum_{v'(v' \neq v)} \langle v|B(r)|v'\rangle^2 / (E_v - E_{v'}), \quad (4)$$

$$A_{D_v} = 2 \sum_{v'(v' \neq v)} \langle v|B(r)|v'\rangle \langle v'|A(r)|v\rangle / (E_v - E_{v'}), \quad (5)$$

$$a_{D_v} = \sum_{v'(v' \neq v)} \langle v|A(r)|v'\rangle^2 / (E_v - E_{v'}), \quad (6)$$

D is the familiar centrifugal distortion constant of rotation arising from the square of the rotation operator $B(r)$. The parameter A_D is due to the cross-term between $A(r)$ and $B(r)$ and contributes to Eq. (3) with the same dependence on J as the rotational part in Eq. (2). Finally, a_D arising from the square of $A(r)$ leads to

a common shift of all rovibrational levels in doublet states. As is evident from Eqs (4)–(6) centrifugal distortion corresponds to a mixing of vibrational levels in the same electronic state.

Approximate formulas for A_D and a_D have already been derived using a power series expansion of $A(r)$ with respect to $(r - r_e)$ and evaluating the matrix elements of Eqs (5) and (6) for the simple case of a harmonic oscillator [8, 9]. These formulas should be valid in particular for the lowest vibrational levels which extend only over the r region near equilibrium. Improved calculations of A_D according to Eq. (5) have been performed, e.g. for the 5 lowest vibrational levels of the $X^2\Pi$ state of OH using again a power series expansion of $A(r)$, but evaluating the required matrix elements from vibrational wavefunctions deduced from the RKR potential [5]. In the case of the $A^2\Pi$ state of NaKr and NaXe experimental data are available only for a limited number of higher vibrational levels covering a fraction of about 1/5 of the whole well depth D_e and being located in the upper part of the well approximately between $0.65 D_e$ and $0.85 D_e$. Therefore, a power series expansion of $A(r)$ around equilibrium seems not to be appropriate, but is also unnecessary in view of the numerical capability of present computers.

In order to calculate A_D and a_D from $A(r)$ a computer program was written for a NeXT computer using C and Fortran 77 as programming language. The input data consist of two files containing $V(r)$ and $A(r)$ for a discrete set of r values. Usually, 5000 points extending over a range between 2 Å and 40 Å turned out to be a sufficient narrow grid. The Schrödinger equation of nuclear vibrational motion in the potential $V(r)$ without rotation was integrated numerically by means of the Numerov–Cooley method [11] providing a set of energy values E_v and wavefunctions $|v\rangle = f_v(r)$ for all bound vibrational levels below dissociation. Using these wavefunctions the program evaluates the required matrix elements $\langle v|A(r)|v'\rangle$ and $\langle v|B(r)|v'\rangle$ by standard integration. Finally, the different contributions from vibrational levels v' with $v' \neq v$ are added according to Eqs (5) and (6). In addition, the program allows the evaluation of the parameters D_v , A_v and B_v .

Before presenting our results in the following Section some remarks concerning the summation in Eqs (4)–(6) are indicated: i) Due to the denominator vibrational levels with $v' > v$ usually contribute with opposite sign compared to levels with $v' < v$. As a result, the final value arises as the difference of two parts about equal in size, but of opposite sign, where each part may distinctly be larger than the final value. Therefore, small changes in one of the main contributions may have a large effect on the final value. ii) Considering vibrational levels with low value of v it is not necessary to extend the sum over v' up to dissociation, as the contribution from the level v' becomes smaller with increasing v' . The sum was terminated in our program, if the contribution of a level v' distinctly fell below the desired limit of accuracy of the final value, e.g. given by the experimental uncertainty of the particular parameter. iii) For vibrational levels v near dissociation the same applies with respect to the contributions of levels with decreasing value of v' . On the other side, the highest bound vibrational level just below dissociation usually contributes a considerable part to the final value and a continuation across the dissociation limit seems to provide non-negligible contributions. Actually, the sum in Eqs. (4)–

(6) should have been extended to the continuum above the dissociation limit. As we have neglected this part in our calculation, our results are not valid for v levels near dissociation. In presenting our results in the next Section we restrict ourselves to v levels where the contribution of the uppermost vibrational level has clearly dropped below the given limit of accuracy.

3. Results and discussion

The starting point of our calculation is the $A\Pi$ interatomic potential as obtained previously from our high-resolution spectroscopic work on NaKr and NaXe [3, 4] assuming a Hund's coupling case (a). Within this work separate potentials $V_{1/2}(r)$ and $V_{3/2}(r)$ have been determined for the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ state, respectively, using the analytical form of a Tang-Toennies or a Thakkar function. Explicit expressions for these two functions may be found as Eqs (7) and (8) in [3]. The interatomic $A\Pi$ potential $V(r)$ in our present calculation was taken as the mean value of $V_{1/2}$ and $V_{3/2}$, whereas the spin-orbit interaction was obtained according to $A(r) = V_{3/2}(r) - V_{1/2}(r)$.

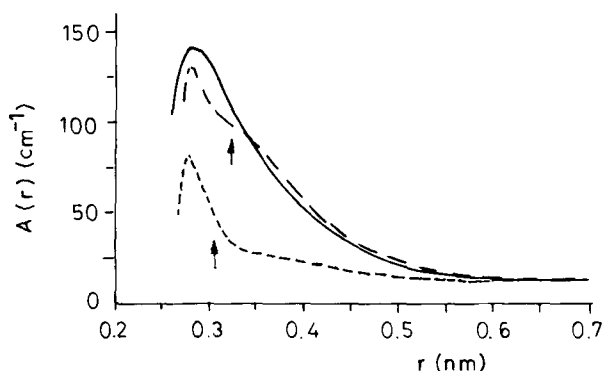


Fig. 1. Spin-orbit interaction as a function of internuclear separation for the $A^2\Pi$ states of Na^{132}Xe and of Na^{84}Kr (solid line: Tang-Toennies NaXe, long dashes: Thakkar NaXe, short dashes: Tang-Toennies NaKr). The arrows indicate the equilibrium position

First, we consider the $A^2\Pi$ state of NaXe. Figure 1 shows our results for $A(r)$ as deduced from our spectroscopic work, where $A(r)$ has been calculated by use of the parameter set given in Table V of [4]. Tables I and II contain our results for the parameters A_{D_v} , a_{D_v} and A_v of molecular spin-orbit interaction calculated from $A(r)$ and $V(r)$ as described in Section 2. In addition, we have included the results for the rotational parameters B_v and D_v . For reasons of conciseness we have

Table I
 Calculated values of A_{D_v} and a_{D_v} in cm^{-1} for $A^2\Pi$ of Na^{132}Xe
 in comparison to experiment. T-T Tang-Toennies potential,
 Thk Thakkar potential

v	$10^3 A_{D_v}$			a_{D_v}	
	T-T	Thk	Exp	T-T	Thk
0	-1.10	-0.45		-1.06	-0.18
2	-1.18	-0.73		-1.11	-0.43
4	-1.29	-1.01		-1.18	-0.71
6	-1.42	-1.28		-1.27	-1.00
8	-1.58	-1.52		-1.37	-1.26
10	-1.75	-1.75	-1.88(2)	-1.48	-1.46
12	-1.94	-1.95	-2.05(2)	-1.57	-1.58
14	-2.13	-2.11	-2.22(2)	-1.62	-1.62
16	-2.27	-2.23	-2.39(2)	-1.60	-1.55
18	-2.31	-2.27		-1.45	-1.40

Table II
 Calculated values of A_v , B_v and D_v in cm^{-1} for $A^2\Pi$ of Na^{132}Xe
 in comparison to experiment. T-T Tang-Toennies potential, Thk Thakkar potential

v	A_v			$10^2 B_v$			$10^7 D_v$		
	T-T	Thk	Exp	T-T	Thk	Exp	T-T	Thk	Exp
0	110.18	100.16		8.261	8.290		2.84	2.74	
2	101.65	96.30		7.875	7.896		3.16	3.11	
4	93.22	90.73		7.475	7.487		3.55	3.53	
6	84.85	83.93		7.060	7.066		4.01	4.02	
8	76.54	76.33		6.629	6.630		4.56	4.59	
10	68.31	68.31	68.35(1)	6.183	6.182	6.181(3)	5.21	5.25	5.62(61)
12	60.21	60.22	60.21(1)	5.722	5.721	5.720(2)	5.98	6.01	6.20(16)
14	52.38	52.37	52.37(1)	5.247	5.248	5.248(2)	6.88	6.91	7.21(16)
16	44.99	45.02	44.91(1)	4.762	4.765	4.762(2)	7.89	7.92	8.41(19)
18	38.22	38.37		4.269	4.273		8.92	8.98	

restricted ourselves to even values of v in the Tables. The experimental data, being available for $v = 10 \dots 16$ for NaXe , are reproduced quite well within limits of error for both types of functions. This is true, in particular, for the first-order parameters A_v and B_v . Slight deviations of the order of 2...5 times the experimental error occur between calculated and observed values of A_{D_v} and D_v , but the deviations do not exceed a margin of 5 % of the value itself. Larger differences are present between the Tang-Toennies and the Thakkar results for the unobserved region of low vibrational levels near equilibrium.

For a qualitative discussion of these observations we refer to the general form of $A(r)$ as depicted in Fig. 1 for the two types of functions. The vibrational motion

for $v = 10 \dots 16$ extends over a range of r values between 0.28 nm and 0.52 nm. The two curves of $A(r)$ are almost identical near the outer turning point which due to its high probability density gives the largest contribution to A_v . Differences between the two curves of the order of $5 \dots 20 \text{ cm}^{-1}$ occur for $0.28 \text{ nm} < r < 0.45 \text{ nm}$, the difference changing sign at about $r = 0.35 \text{ nm}$. Obviously, the higher value of $A(r)$ for the Tang-Toennies case in comparison to the Thakkar potential for $0.28 \text{ nm} < r < 0.35 \text{ nm}$ is completely compensated by a corresponding lower value within $0.35 \text{ nm} < r < 0.45 \text{ nm}$ to yield almost identical values of A_v for $v = 10 \dots 16$. However, no such compensation is to be expected near equilibrium leading to different values of A_v for low vibrational states. Incidentally, both curves of $A(r)$ in Fig. 1 show a negative slope at equilibrium, thus explaining the negative sign of A_D according to our simple classical argument. In addition, both curves pass through a maximum around $r = 0.28 \text{ nm}$. However, the further structure of $A(r)$ for smaller values of r cannot be predicted reliably from our work. As the experimental data are reproduced equally well by the two types of functions, the observed difference in $A(r)$ should be considered as an estimate of the accuracy in determining $A(r)$ from spectroscopic data.

According to Table I the absolute values of A_{D_v} of NaXe increase continuously with increasing v for both types of functions in agreement with experimental observation. With respect to a_{D_v} , the absolute values are likewise increasing for the lower vibrational levels, but pass through a maximum around $v = 14$. It is the difference between a_{D_v} values of subsequent vibrational levels which is inevitably included in the experimentally determined vibrational spacings $E_{v+1} - E_v$ which mainly fix the structure of the interatomic potential. From Table I and Eq. (3) we deduce an upper limit of 0.01 cm^{-1} for the contribution of the difference in a_{D_v} to $E_{v+1} - E_v$ within the experimentally observed region of $v = 10 \dots 16$. As this upper limit is about equal to the experimental error of $E_{v+1} - E_v$, the effect of a_{D_v} may be neglected in determining $V(r)$ for the case of the $A\Pi$ state of NaXe.

As has been known for a long time, the parameter A_D is almost completely correlated with the coupling constant γ of spin-rotation interaction in a molecular ${}^2\Pi$ state [12, 13]. The parameter deduced from experimental line positions must be considered as an effective parameter \tilde{A}_D being connected with A_D and γ by means of the relation

$$\tilde{A}_D = A_D - 2\gamma B / (A - 2B). \quad (7)$$

In order to check the effect of γ on \tilde{A}_D we have used the van Vleck approximation of $\gamma = -m_e A / 2\mu$ (m_e electron mass, μ reduced mass of the nuclei, A molecular spin-orbit splitting) yielding an upper limit for the size of γ [14]. Inserting numbers into Eq. (7) the part due to γ turns out to be distinctly smaller than the experimental error of \tilde{A}_D for the case of the $A\Pi$ states of NaKr and NaXe. Therefore, we are allowed to identify the experimentally observed effective parameter \tilde{A}_D with A_D for both molecules.

Finally, we turn to a discussion of our results for the $A\Pi$ state of NaKr which are compiled for the parameters A_{D_v} and a_{D_v} in Table III. The experimentally observed region extends from $v = 7$ to $v = 14$ covering a range of internuclear

Table III
 Calculated values of A_{D_v} and a_{D_v} in cm^{-1} for $A^2\Pi$ of Na^{84}Kr
 in comparison to experiment. T-T Tang-Toennies potential,
 Thk Thakkar potential

v	$10^3 A_{D_v}$			a_{D_v}	
	T-T	Thk	Exp	T-T	Thk
0	-1.82	-0.65		-1.42	-0.18
2	-1.21	-0.64		-0.48	-0.15
4	-0.91	-0.71		-0.16	-0.16
6	-0.87	-0.83		-0.09	-0.19
8	-0.99	-0.98	-1.34(1)	-0.12	-0.22
10	-1.11	-1.13	-1.47(1)	-0.15	-0.24
12	-1.12	-1.24	-1.56(1)	-0.12	-0.23
14	-0.88	-1.23	-1.56(1)	0	-0.18
16	-0.21	-0.94		+0.21	-0.08

distances between 0.27 nm and 0.54 nm. Again, the two types of Tang-Toennies and Thakkar analytical functions have been used, reproducing the experimental energy levels equally well within error margins [3]. Figure 1 contains our result for $A(r)$ for the Tang-Toennies function as deduced from the parameter set given in Table VI of [3] for fixed dissociation limit. The general form of $A(r)$ is similar to the case of NaXe. However, the absolute values of $A(r)$ are considerably smaller for NaKr than for NaXe in accordance with the smaller experimental values of A_v .

According to Table III the calculated values of A_{D_v} agree with the experimental results only qualitatively for both types of functions, the difference being about 30 %. In addition, the absolute values of A_{D_v} do not show the smooth behaviour with increasing v as for the case of NaXe. However, for both functions our calculation predicts a maximum for the absolute value of A_{D_v} around $v = 12$ which seems to be also present within the experimental data. With respect to a_{D_v} the absolute values of Table III are considerably smaller than for the case of NaXe, as expected from the size of $A(r)$ discussed above, and may again be neglected in determining $V(r)$. Incidentally, the calculated values of A_v also show slight deviations from the experimental values for the case of NaKr. Most probably, the nearby $B^2\Sigma$ state, being coupled by spin-orbit interaction to the $\Pi_{1/2}$ substate and being neglected in our present work, has a larger effect in the case of NaKr than for NaXe, as the upper observed vibrational levels are closer to dissociation in the former case.

4. Conclusion

Second-order perturbation theory has been used in order to calculate the parameters A_D and a_D of molecular spin-orbit interaction for the $A^2\Pi$ states of NaKr and NaXe. The calculated values of A_D are in good agreement with the experimental results for the case of NaXe. Poorer agreement within a margin of 30 % is achieved for NaKr. As A_D samples an extended region of interatomic

distances in comparison to A_v , our calculations support the correctness of the spin-orbit operator $A(r)$ deduced from high-resolution spectroscopic data. In addition, our results show, that the effect of a_D may safely be neglected in deducing $V(r)$ from spectroscopic data at the present level of accuracy.

Several improvements could be applied to the method of approach used in our present work, in particular if vibrational levels near dissociation are considered. On the one side, the effect of the dissociation continuum should be taken into account. On the other hand, due to the non-diagonal part of the spin-orbit interaction the nearby $B^2\Sigma$ state affects the interatomic potential of the $A^2\Pi_{1/2}$ state shifting the energy values of the vibrational levels. This shift should be taken into account in deducing $A(r)$ from spectroscopic data. We are currently performing such a calculation for the case of the $A^2\Pi$ state of KAr.

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