

Rotational magnetic moment of the Na₂ molecule in A ¹Σ_u⁺ state: Perturbation effects

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Values and signs of Landè factors (g) have been measured for four rovibronic levels of the A ¹Σ_u⁺ state of the Na₂ molecule. Because of a very small product $g\tau \sim 10^{-12}$ s, the level crossing signal of a dispersion shape was employed using circular light polarization and mutually orthogonal excitation, observation of laser induced fluorescence, and external magnetic field directions. The effects of the $b^3\Pi_u$, $B^1\Pi_u$, and $a^3\Sigma_u^+$ states on the g factors of the Na₂ (A ¹Σ_u⁺), as well as their dependence on vibrational and rotational quantum numbers, have been theoretically analyzed. An analytical connection has been found between the constants of Λ doubling (q) and Landè factors of the interacting singlet states. Simple expressions have been found for estimating the effects of distant electronic states on q and the g factors without summing over bounded and integrating over continuum levels of the perturbing state.

I. INTRODUCTION

The Na₂ molecule has been used for many years as a test molecule for spectroscopic theory and techniques. The first excited singlet state A ¹Σ_u⁺ and the second excited triplet state $b^3\Pi_u$ have been known to interact for a long time.¹⁻³ One of the most obvious manifestations of this interaction is the disturbance in the regular structure of the rotational bands, as observed both in emission and absorption. It is hardly surprising therefore that high-resolution spectroscopy is employed for studying such perturbations, since it makes it possible to determine small divergences in the position of rovibronic levels in the interacting electronic states. In the course of the past ten years, a number of laser spectroscopic methods have evolved which make it possible to obtain highly resolved spectra. These methods have been successfully employed for studying the A ¹Σ_u⁺ and $b^3\Pi_u$ states and their interaction.⁴⁻⁸

It is rather obvious that any perturbation affects not only the energy of the states, but also their wave functions. This naturally leads to changes in other affiliated molecular characteristics, such as radiational and magnetic properties.²⁻⁹

The present study deals with some peculiarities in the effects of A ¹Σ_u⁺-B ¹Π_u, A ¹Σ_u⁺- $b^3\Pi_u$, and A ¹Σ_u⁺- $b^3\Pi_u$ - $a^3\Sigma_u^+$ interactions on the rotational magnetic moment of the A state by means of determining Landè factors for a number of rovibronic levels of A state.

It ought to be noted that the method proposed for studying molecular perturbations¹⁰ does not require such high spectral resolving power, as is necessary in the experiments based solely on the measurements of the positions of rovibronic energy levels. The main advantage, however, of the use of Landè factors for studying perturbations of diamagnetic ($\Omega = 0$) states is their extreme sensitivity to the value and type of not only local, but also of regular interactions. This is

easily understood, if one keeps in mind that a nonperturbed diamagnetic state possesses a near zero magnetic moment, which is independent of vibrational and rotational quantum numbers. Accordingly, any, even small, perturbation due to paramagnetic electronic states leads to drastic relative changes of the magnetic moment value. This in turn is easily observed experimentally, since modern methods permit Landè factor measurements of the order of (10^{-4} - 10^{-5}).^{11,12} It may also be noted that the sign of the Landè factors is an additional source of information on the type of perturbation.¹³

The present work consists of the study of the basic causes of the appearance of a nonzero magnetic moment in the diamagnetic A ¹Σ_u⁺ state, as well as the calculation of the dependence of the g factors on vibrational and rotation quantum number values, and finally, performing experimental testing of results on a number of rovibronic levels of Na₂ (A ¹Σ_u⁺). Although the viability of the above statements can manifest itself most fully only in systematic g factor measurements over a large group of rovibronic levels of the A ¹Σ_u⁺ state, we have undertaken, by way of a first stage, measurements of four well known¹⁴ v, J levels, excited by the 632.8 nm He-Ne laser line. An initial report on the results obtained can be found in Ref. 15. For these levels the product $g\tau$ value is extremely small ($\sim 10^{-13}$ - 10^{-12} s). To avoid the usage of very large magnetic field, we developed a special kind of method based on Hanle effect in laser induced fluorescence under circularly polarized excitation and mutually orthogonal excitation, observation and magnetic field directions. For ¹Σ-¹Σ transitions of P, R type, this leads to Hanle signal of dispersion shape having the greatest steepness when the magnetic field strength is equal to zero.

Expected Landè factors for Na₂ (A ¹Σ_u⁺) were located taking into account the "nuclear" contribution caused by the rotation of shielded sodium atom cores as well as the electronic part connected with A ¹Σ_u⁺- $b^3\Pi_u$ and A ¹Σ_u⁺-B ¹Π_u mixing. It is shown that in this concrete situation one can neglect the influence of the $a^3\Sigma_u^+$ state as well

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as the role of the second order perturbation effects according to magnetic field strength. The interaction between the states $A^1\Sigma_u^+$ and $B^1\Pi_u$ has been used for analyzing the possibility of employing Landé factors for investigating structural and magnetic properties of mutually distant electronic terms, and that between the states $A^1\Sigma_u^+$ and $b^3\Pi_u$ for investigating local perturbations caused by the crossing terms.

II. EXPERIMENT

A. Method of measurement

The experimental determination of the g -factor values in Na₂ ($A^1\Sigma_u^+$ state) is connected with certain difficulties. Indeed, application of optomagnetic methods of measurements requires that the product $\omega\tau$, where ω is the frequency of magnetic splitting, should have a value of the order of (or larger than) unity. If we consider that τ in the case of Na₂ ($A^1\Sigma_u^+$) has a characteristic value of 12.5 ns (Ref. 16), then the condition $\omega\tau = 1$ corresponds to magnetic fields of the order of $B = \hbar/(\mu_B g \omega \tau) = 10\text{--}20$ T, which by far exceeds the possibilities of the electromagnet at our disposal. However, a certain chance of measuring the Landé factor under conditions when $\omega\tau$ lies considerably below unity value can be obtained by applying the Hanle effect in a variant implying a "dispersion shape" of signal. Such a variant of the method yielding information both on the value and the sign of the g factor, as far as we know, has been used with linearly polarized excitation, see e.g., Refs. 17–19.

Let us consider the fluorescence in the cycle $J_i'' \rightarrow J_e' \rightarrow J_f''$ (Fig. 1), excited by directed light with a given polarization \hat{E} . In order to describe the effect of the magnetic field on polarization we shall apply a treatment in terms of polarization moments, e.g., Refs. 20–22. The intensity $I(\hat{E}')$ of given polarization \hat{E}' propagating in a definite direction on transition $J_e' \rightarrow J_f''$ may be represented, according to Ref. 21 in the following form:

$$I(\hat{E}') = (-1)^{J_e' + J_f''} (2J_e' + 1)^{1/2} I_0 \times \sum_{K=0}^2 (2K+1) \begin{Bmatrix} 1 & 1 & K \\ J_e' & J_e' & J_f'' \end{Bmatrix} \times \sum_{Q=-K}^K (-1)^Q f_Q^K \Phi_{-Q}^K(\hat{E}'). \quad (1)$$

Here $\left\{ \begin{matrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{matrix} \right\}$ is a 6j-symbol, f_Q^K —the polarization moment of state $|J_e'\rangle$, K —its rank, while its projection Q varies from $-K$ to K . The tensor $\Phi_{-Q}^K(\hat{E}')$ has been introduced in Ref.

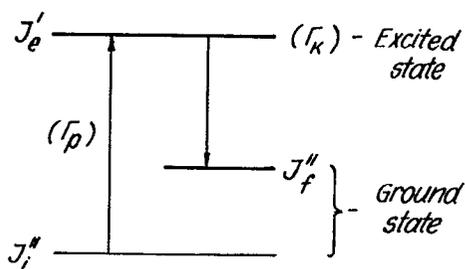


FIG. 1. Optical transition scheme.

21 and it characterizes the polarization of light. Its components may be calculated through the cyclic components E^Q of the polarization vector \hat{E}' as

$$\Phi_Q^K(\hat{E}') = (2K+1)^{-1/2} \times \sum_{Q', Q''=-1}^1 (-1)^{Q''} E^{Q'} (E^{Q''})^* C_{1-Q', 1Q''}^K \quad (2)$$

using Clebsch–Gordan coefficients $C_{\alpha\beta\gamma}^{\epsilon}$. The necessary values of Φ_Q^K can be found in table form, e.g., in Ref. 23. The polarization moments f_Q^K formed by the light in the act of absorption $J_i'' \rightarrow J_e'$, (Fig. 1) proceeding at the rate Γ_p in the presence of an external magnetic field \mathbf{B} can be calculated as follows:

$$f_Q^K = (-1)^{J_e' + J_i''} \Gamma_p (\Gamma_K - iQ\omega)^{-1} (2J_e' + 1)^{3/2} \times (2J_i'' + 1)^{-1} \begin{Bmatrix} 1 & 1 & K \\ J_e' & J_e' & J_i'' \end{Bmatrix} \Phi_Q^K(\hat{E}') n_{J_i''}, \quad (3)$$

where $n_{J_i''}$ is the concentration of absorbing molecules, Γ_K is the relaxation rate of the moment of rank K (under assumption of $\Gamma_p \ll \Gamma_K$), but $\Phi_Q^K(\hat{E}')$ characterizes the polarization of the exciting radiation.

The Hanle effect is traditionally recorded with linearly polarized excitation [Figs. 2, 3(a), and 3(b)] with magnetic field $\mathbf{B} \perp \hat{E}$, while observation takes place along the Z axis. The signal is observed through the degree of linear polarization \mathcal{P} from the intensities of orthogonally polarized components $I_1 = I_\varphi, I_2 = I_{\varphi + \pi/2}$, which can easily be expressed through f_2^2, f_0^2 , and f_0^0 (e.g., Ref. 24)

$$\mathcal{P}(\chi) = \frac{I_1 - I_2}{I_1 + I_2} = -\mathcal{P}(0) \frac{\cos 2\varphi + 2\chi \sin 2\varphi}{1 + 4\chi^2}, \quad (4)$$

$$\chi = \omega/\Gamma_2.$$

Here $\mathcal{P}(0)$ denotes the degree of polarization of fluorescence, as it would be at $\varphi = \pi/2, \chi = 0$, i.e., in the absence of

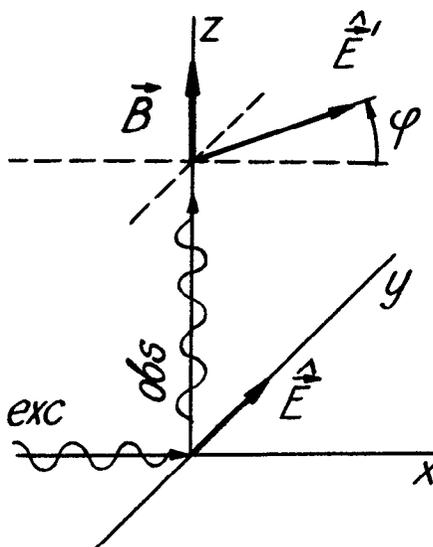


FIG. 2. Experimental geometry for linear polarized excitation (\hat{E}) and observation (\hat{E}').

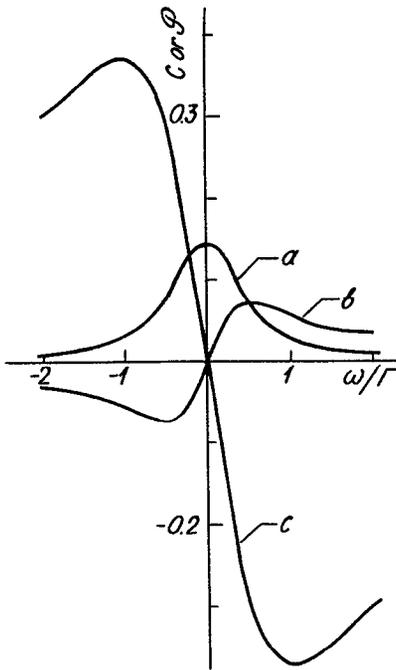


FIG. 3. Calculated Hanle signal curves. (a) linear polarized excitation (Fig. 2), $\varphi = \pi/2$ in Eq. (4); (b) the same conditions, except $\varphi = \pi/4$; (c) circularly polarized excitation (Fig. 4), cf. Eq. (8).

magnetic field. In the $J \rightarrow \infty$ limit the known²⁴ $\mathcal{P}(0)$ values are $1/7$ for (P, R) \uparrow, \downarrow and $1/2$ for $Q \uparrow, Q \downarrow$ transitions (here the arrows \uparrow or \downarrow denote absorption or emission). In order to ascertain the possibility of observing a Hanle signal at $\chi \ll 1$, let us examine the behavior of the derivative

$$\frac{d\mathcal{P}}{d\chi} = -\mathcal{P}(0) \times \frac{2 \sin 2\varphi(1 + 4\chi^2) - (\cos 2\varphi - 2\chi \sin 2\varphi)8\chi}{(1 + 4\chi^2)^2} \quad (5)$$

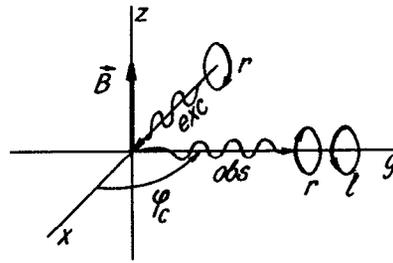


FIG. 4. Experimental geometry for circularly polarized excitation.

If $\varphi = 0$, then the derivative becomes zero at $\chi \rightarrow 0$. Hence the traditionally most frequently observed signal is of Lorentzian shape $\mathcal{P}(\chi) = \mathcal{P}(0)/(1 + 4\chi^2)$, dating back from Hanle's time,²⁵ Fig. 3(a). On the other hand, we get the largest value of $d\mathcal{P}/d\chi$ in the vicinity of $\chi = 0$ for $\varphi = \pi/4$, when the slope of the straight line equals $2\mathcal{P}(0)$, Fig. 3(b).

For Q -type transitions such conditions are, indeed, optimal, since $2\mathcal{P}(0) = 1$ at $J \rightarrow \infty$. At the same time, we get $2\mathcal{P}(0) = 2/7$ for P or R transitions, i.e., just the ones that take place in the $^1\Sigma^-^1\Sigma$ system of Na₂. As it turns out, one can find more advantageous conditions in this case. Let excitation, polarized along a right-hand circle, take place, as shown in Fig. 4. Let us now follow the degree of circularity

$$C = (I_r - I_l)/(I_r + I_l) \quad (6)$$

by measuring, at right angles to the field B direction,²⁶ the intensity I_r, I_l , polarized along the right-hand (I_r) or left-hand (I_l) circle. The value of C for arbitrary angles φ_c between the excitation and observation directions, see Fig. 4, can be expressed through $f_1^1, f_2^2, f_0^2, f_0^0$ as

$$C = \frac{\begin{Bmatrix} 1 & 1 & 1 \\ J_e' & J_e' & J_f'' \end{Bmatrix} \text{Re}(e^{-i\varphi_c f_1^1})}{-(1/3) \begin{Bmatrix} 1 & 1 & 0 \\ J_e' & J_e' & J_f'' \end{Bmatrix} f_0^0 + \begin{Bmatrix} 1 & 1 & 2 \\ J_e' & J_e' & J_f'' \end{Bmatrix} [(1/6)\sqrt{5/2}f_0^2 - (1/2)\sqrt{5/3} \text{Re}(e^{-2i\varphi_c f_2^2})]} \quad (7)$$

Substituting f_Q^K from Eq. (3), we obtain

$$C = \frac{36 \begin{Bmatrix} 1 & 1 & 1 \\ J_e' & J_e' & J_f'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ J_e' & J_e' & J_f'' \end{Bmatrix} (\Gamma_0/\Gamma_1) (\cos \varphi_c + \chi \sin \varphi_c) / (1 + \chi^2)}{[8(-1)^{J_f'' - J_e'} / (2J_e' + 1)] + \begin{Bmatrix} 1 & 1 & 2 \\ J_e' & J_e' & J_f'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ J_e' & J_e' & J_f'' \end{Bmatrix} (\Gamma_0/\Gamma_2) [3 + 9(\cos 2\varphi_c + 2\chi \sin 2\varphi_c) / (1 + 4\chi^2)]} \quad (8)$$

The necessary values of the $6j$ -symbols are

$$\begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J \end{Bmatrix} = \begin{cases} J' - J = -1(P); & \frac{1}{2} \left[\frac{2J'}{(2J'+1)(J'+1)3} \right]^{1/2} \\ J' - J = 0(Q); & \frac{1}{2} \left[\frac{2}{J'(2J'+1)(J'+1)3} \right]^{1/2} \\ J' - 1 = 1(R); & (-1)^{2J'+1} \frac{1}{2} \left[\frac{2(J'+1)}{J'(2J'+1)3} \right]^{1/2} \end{cases} \quad (9)$$

The signal we are interested in will be determined by the derivative, which in the $J' \rightarrow \infty$ limit for P, R transitions is as follows:

$$\left. \frac{dC}{d\chi} \right|_{\chi=0} = \pm 60 \frac{\sin \varphi_C (81 + 3 \cos 2\varphi_C) - 6 \cos \varphi_C \sin 2\varphi_C}{(81 + 3 \cos 2\varphi_C)^2} \quad (10)$$

The derivative assumes zero value at $\varphi_C = 0$. Its maximum value is attained in the case $\varphi_C = \pi/2$, as shown in Fig. 4, being equal to $\pm 10/13$, which exceeds the value for linear polarization by a factor of almost 3. Thus maximum slope of the Hanle signal can be achieved in the region of $\chi = 0$, cf. Fig. 3(c). This provides a new possibility to measure the g -factor values in conditions when $\omega\tau \ll 1$. An additional advantage consists in the fact that this situation provides the most favorable geometry for collecting fluorescence from the cell in the gap of the electromagnet, since observation is performed at right angles with respect to the direction of the magnetic field (Fig. 4). Unlike the situation in Fig. 2, here we have no problem of deflecting the fluorescent beam in order to direct it out the gap of the electromagnet.

B. Experimental details

Metallic sodium was placed into a glass cell joined to the vacuum system by means of a dry valve. The optical part of the cell was positioned in the gap of the electromagnet (up to 1 T) of 40 mm width. The saturating sodium vapor was at a

temperature of 550–630 K, which corresponds to a content of $[\text{Na}] = 1\text{--}16 \times 10^{14} \text{ cm}^{-3}$, $[\text{Na}_2] = 7\text{--}240 \times 10^{11} \text{ cm}^{-3}$.²⁷ The exciting light from a He–Ne laser was cut down to a power of ~ 1 mW in order to avoid nonlinear effects of optical pumping of the lower state,²⁸ since at a working power of ~ 49 mW a nonlinear Hanle effect of the lower state had been observed of ~ 0.2 T half-width that is similar to the results in Ref. 29.

Convenient working lines of the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ fluorescence spectrum corresponding to the v', J' levels (Table I) were selected out by means of a double diffraction monochromator (5 Å/mm). The degree of linear polarization or circularity was measured in the following way. The entrance slit of the spectrometer was divided in height into two parts, and two orthogonal analyzers were placed in front of them. Light guides conducted the light from two respective parts of the exit slit of the monochromator to the two photomultipliers, which counted simultaneously one-photon pulses from two channels. Circular polarization was provided by inserting two mica quarter-wave plates.

C. Results

Dispersion-shaped initial parts of Hanle signals in the regions $\omega/\Gamma \ll 1$, as obtained within the $B = \pm 1$ T range were of rather insignificant magnitude at linear polarization of light. However, they made it possible to obtain a preliminary estimate of the g factors for Na₂ ($A^1\Sigma_u^+$), as well as to determine their sign. More definite results were obtained from signals received in an arrangement according to Fig. 4

TABLE I. Calculated mixing coefficients S_{11} , S_x and g factors for rovibronic states of Na₂ ($A^1\Sigma_u^+, v', J'$) involved in this work. Here $g_{v', J'}^{A^1\Sigma_u^+}(b^3\Pi_u)$ and $g_{v', J'}^{A^1\Sigma_u^+}(B^1\Pi_u)$ denote the corresponding parts due to $A^1\Sigma_u^+ - b^3\Pi_u$ or $A^1\Sigma_u^+ - B^1\Pi_u$ interaction, $g_{v', J'}^{\text{th}}(\text{tot}) = g_{v', J'}^{A^1\Sigma_u^+}(b^3\Pi_u) + g_{v', J'}^{A^1\Sigma_u^+}(B^1\Pi_u) + g_n$, while $g_{v', J'}^{\text{exp}}$ are experimentally measured values.

	$v' = 14, J' = 45$	$v' = 22, J' = 86$	$v' = 25, J' = 87$	$v' = 16, J' = 17$
S_{10}	4.56×10^{-2}	-1.64×10^{-3}	-8.06×10^{-5}	6.17×10^{-3}
S_{11}	-2.42×10^{-2}	-5.07×10^{-2}	4.77×10^{-2}	-7.74×10^{-4}
S_{12}	1.38×10^{-2}	-4.11×10^{-2}	-5.78×10^{-2}	1.23×10^{-4}
S_x	9.98×10^{-1}	9.98×10^{-1}	9.97×10^{-1}	1.0000
$g_{v', J'}^{A^1\Sigma_u^+}(b^3\Pi_u)$	8.88×10^{-5}	-7.21×10^{-5}	8.32×10^{-5}	7.86×10^{-7}
$g_{v', J'}^{A^1\Sigma_u^+}(B^1\Pi_u)$	-7.32×10^{-5}	-6.88×10^{-5}	-6.84×10^{-5}	-7.44×10^{-5}
$g_{v', J'}^{\text{th}}(\text{tot})$	$+3.95 \times 10^{-5}$	-11.7×10^{-5}	$+3.87 \times 10^{-5}$	-5.05×10^{-5}
$g_{v', J'}^{\text{exp}}$	$+3.13 \times 10^{-5}$	-13.6×10^{-5}	$+2.41 \times 10^{-5}$	-5.32×10^{-5}

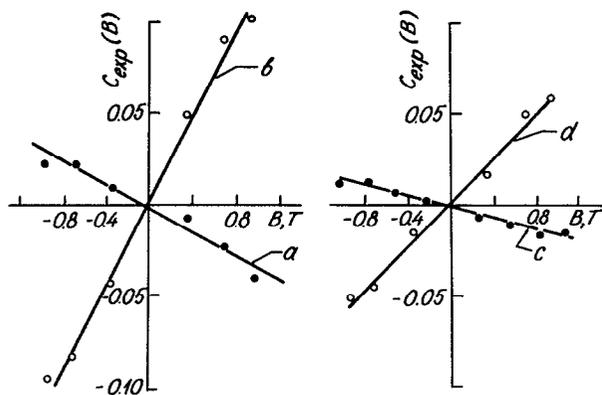


FIG. 5. Magnetic field dependence for the degree of circularity C measured using the geometry shown in Fig. 4. The quantum numbers involved in a transition $(v'', J'') \rightarrow (v', J')$ are as follows: (a) $(2, 46) \rightarrow (14, 45)$; (b) $(6, 85) \rightarrow (22, 86)$; (c) $(8, 86) \rightarrow (25, 87)$; (d) $(4, 18) \rightarrow (16, 17)$.

($\varphi_C = \pi/2$). Examples of $C_{\text{exp}}(B)$ dependences obtained are presented in Fig. 5. Satisfactory accuracy within the given ω/Γ range can be achieved by approximating the results obtained by straight lines

$$\left. \frac{dC}{d\chi} \right|_{\chi=0} = \begin{cases} \pm \frac{6}{8(J'+1)/J' - (1/5)(2J'-1)/(2J'+3)}, & (P \uparrow, P \downarrow) \\ \pm \frac{6}{8J'/(J'+1) - (1/5)(2J'+3)/(2J'-1)}, & (R \uparrow, R \downarrow) \end{cases} \quad (12)$$

This yields $(dC/d\chi)_{\chi=0}$ values of 0.7236 ($J' = 17$), and 0.7513 ($J' = 45$), as opposed to the value of $10/13 = 0.7692$ ($J' \rightarrow \infty$). The relaxation constant Γ was found through the time of spontaneous decay. This lies within the range of $\tau_{\text{sp}} = 12.45\text{--}12.50$ ns¹⁶ for the v', J' levels of Na₂ ($A^1\Sigma_u^+$) included in the present discussion. The contribution of collisions at the working concentrations of vapors is expected to be insignificant. It was accounted for, assuming, as a fair estimate, a quenching cross section of 5×10^{-14} cm², as given in Ref. 30 for Na₂ ($B^1\Pi_u$)–Na collisions, leading to an increase in Γ by 4% with respect to τ_{sp}^{-1} .

The g -factor values obtained from the above procedure, as averaged over a number of experimental trials, are presented in Table I. The relative error of the values obtained was estimated to be 15%.

III. CAUSES FOR THE APPEARANCE OF A NONZERO ROTATIONAL MAGNETIC MOMENT IN THE $A^1\Sigma_u^+$ STATE OF Na₂

The Landé factor (g) of a diatomic molecule is well known to consist of a nuclear contribution (g_n) caused by the rotation of the nuclear core of the molecule, and of the electronic contribution ($g_{e,J}$) created by the electronic shell of the rotating molecule.³¹ In the case of a diamagnetic electronic state, as we have it in the $A^1\Sigma_u^+$ state ($\Omega = 0$) of Na₂, the electronic contribution is exclusively due to interaction

$$C_{\text{exp}}(B) = a \left(\frac{dC}{d\chi} \right)_{\chi=0} g_{v', J'}^{\text{exp}} \mu_B B / \hbar \Gamma + \delta. \quad (11)$$

For better fit the term δ is introduced to compensate for the residual errors of calibrating the channels. The data in Fig. 5 are normalized allowing for condition $\delta = 0$ for better clarity. The correcting coefficient a , which is close to unity, accounts for the depolarizing effect of the optical channel. Its value was found from results of testing the setup. For $R \uparrow, P \downarrow$ or $P \uparrow, R \downarrow$ transitions, which took place in the cases represented in Fig. 5, the value $(dC/d\chi)_{\chi=0} = \pm 10/13$ was assumed, as obtained for $J \rightarrow \infty$. This may be done, since it is well known²⁴ that for this type of transition the values of the degree of circularity do not depend on J . In the case when circularity was measured for the second component of the doublet, which would correspond to $P \uparrow, P \downarrow$ or $R \uparrow, R \downarrow$ transitions, use of expression (10) leads to a certain error, which becomes particularly significant for $J'_e \equiv J' = 17$. Therefore, one must use, in such cases, values of the derivative $dC/d\chi$ for arbitrary J values, as obtained by employing expressions (1)–(3) and (6)–(9). At $\varphi_C = \pm \pi/2$ they are of the form

of the given state with other electronic states which themselves possess a nonzero magnetic moment.

Obviously, the degree of the effect of different electronic states on the magnetic properties of the $A^1\Sigma_u^+$ state is determined by the ratio between the interaction matrix element value and the distance between the interacting states. Considering this circumstance, as well as the necessity of paramagnetism of the perturbing state, as well as the $u \leftrightarrow u$ selection rules, it becomes possible to select the basic electronic states, interaction with which leads to the appearance of a nonzero magnetic moment in the $A^1\Sigma_u^+$ state. The relative positions of potential curves employed in the present work are presented in Fig. 6.

A. Calculation of the nuclear contribution (g_n)

For a homonuclear diatomic molecule the value of the nuclear contribution is given by the expression^{32–34}

$$g_n = \frac{\mu_n}{\mu_B} \frac{Z_{\text{eff}}^*}{M_n}, \quad (13)$$

where M_n is the mass of the atom forming the molecule. Here μ_B and μ_n are the Bohr and nuclear magnetons, and Z_{eff}^* is the effective nuclear charge produced by the atomic core screened by the internal “nonvalence” atomic shell. The value of Z_{eff}^* is obviously not known *a priori*. Its calculation requires knowledge of the electronic wave functions of

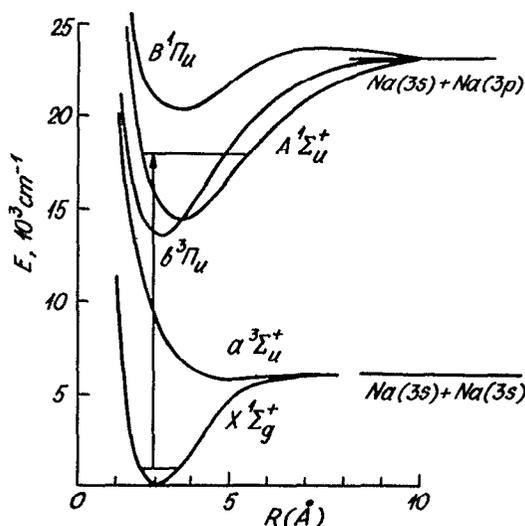


FIG. 6. Potential curves for the electronic states of Na₂ molecule considered in this work.

the molecule. Nevertheless, using a number of simplified model notions on the electronic structure of the given molecule, the value of Z_{eff}^* may be tentatively estimated. Thus, assuming that the electronic structure of alkali metal dimers is hydrogenlike, i.e., assuming that in the formation of the dimer only one external valence electron takes part from each atom, and assuming further that the structure of the internal shells of the atoms does not undergo any change in the transition from isolated atoms to a molecule, one may conclude that the value of Z_{eff}^* for them must be close to unity. In that case the value of the nuclear contribution for the Na₂ molecule must equal 2.4×10^{-5} (in Bohr magnetons).

The viability of the given model of accounting for the nuclear contribution is supported by the fair coincidence between calculated and measured rotational magnetic moment values for the electronic ground states of alkali metal dimers.³⁴ It ought to be stressed that the nuclear contribution is always positive and does not depend on vibrational and rotational quantum numbers. It appears also to change little from one electronic state to another.

B. Effect of $^1\Sigma-^3\Pi$ interaction on the Landè factors of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states

Let us first consider in a general way the effect of $^1\Sigma-^3\Pi$ perturbation on the Landè factors of interacting states of a diatomic molecule. After that we shall analyze in detail the peculiarities of its manifestation in the case of concrete rovibronic levels of $A^1\Sigma_u^+$ and $b^3\Pi_u$ states of the Na₂ molecule.

We shall represent the total wave function Ψ_i of the states under consideration in the form of a linear combination of nonperturbed wave functions corresponding to a "pure" Hund's case a

$$\Psi_i = S_\Sigma |\Sigma\rangle + S_{\Pi_0} |^3\Pi_0\rangle + S_{\Pi_1} |^3\Pi_1\rangle + S_{\Pi_2} |^3\Pi_2\rangle, \quad (14)$$

and the nonzero interaction matrix elements between $^1\Sigma$ and

$^3\Pi_0$, $^3\Pi_1$ components of the $^3\Pi$ state, after Kovács³⁵ in the form

$$H_{\Sigma\Pi_0} \equiv \xi \approx \xi_{el} \langle v_\Sigma | v_{\Pi_0} \rangle, \quad (15a)$$

$$H_{\Sigma\Pi_1} = \gamma_{el} \langle v_\Sigma | v_{\Pi_1} \rangle [J(J+1)]^{1/2}, \quad (15b)$$

where v_Σ , v_Π are vibrational quantum numbers and J denotes the rotational quantum number that must be equal for both interacting states. The strongest $^1\Sigma-^3\Pi$ interaction is due to the spin-orbit interaction operator $\sum_k a_k l_k s_k$, where the summation is over all valence electrons. This interaction connects the $^1\Sigma$ and the $^3\Pi_0$ components and does not depend on J in explicit form, but does depend on the overlap integral between the vibrational wave functions $|v_\Sigma\rangle$ and $|v_{\Pi_0}\rangle$ of the interacting states. The nonzero matrix element of interaction between the $^1\Sigma$ and $^3\Pi_1$ component appears by virtue of the operator terms $-[1/(2\mu R^2)] \times (J-L^+ + J^+L^-)$, where μ is the reduced mass, and R the internuclear distance (in atomic units). It is assumed here that the pure Hund's case a is disturbed, and the quantum number S of the spin vector \mathbf{S} is no longer a good one.³⁶ The value of the matrix element $H_{\Sigma\Pi_1}$ for the molecules following pure Hund's case a must obviously be smaller than $H_{\Sigma\Pi_0}$. This appears to hold for such light molecules as Li₂ and Na₂.

An expression for the g factors of the states under discussion can be obtained from averaging the Zeeman operator $\hat{H}_Z = \mu_B \hat{B}(\hat{L} + 2\hat{S})$,³⁷ where \hat{B} is the magnetic field operator, over the total wave functions Ψ_i , cf. Eq. (14). Then, using the expressions for the matrix elements of operator \hat{H}_Z acting on the basic wave functions, and corresponding to Hund's case a we find, in first-order perturbation theory³²

$$g_{\omega}^e = -[J(J+1)]^{-1} \{ (S_{\Pi_1}^2 + 4S_{\Pi_0}^2) + 2\sqrt{2}S_{\Pi_1} [S_{\Pi_0}\sqrt{J(J+1)} + S_{\Pi_2}\sqrt{J(J+1)-2}] + 2S_\Sigma S_{\Pi_1} \sqrt{J(J+1)} \eta_{el} \langle v_\Sigma | v_{\Pi_1} \rangle \}, \quad (16a)$$

where

$$\eta_{el} = \langle ^3\Pi_1 | l^+ + 2s^+ | ^1\Sigma \rangle. \quad (16b)$$

Expression (16) is valid for describing Landè factors for the $^1\Sigma$ state, as well as for each component of the $^3\Pi$ state. Thus in absence of $^1\Sigma-^3\Pi$ interaction ($S_\Sigma = 0$), formula (16) gets transformed into the well known expression for the g factor of the nonperturbed $^3\Pi$ state.³² The characteristic dependence of Landè factors of each component of the nonperturbed $b^3\Pi_u$ state of Na₂ on the rotational quantum number J is represented in Fig. 7. It ought to be noted that the values of the g_{ω}^e factors are practically independent of the vibrational quantum number v .

The value of the electronic matrix element η_{el} , similar to γ_{el} from Eq. (15b), must theoretically tend towards zero in the case of closeness of the electronic states under consideration to pure Hund's case a or b. One may, accordingly, easily neglect the last terms in Eq. (16a) for such light molecules as Li₂ and Na₂. With this in mind, we obtain a simple expression for the Landè factor of the perturbed $^1\Sigma$ state

$$g_{\omega}^{\Sigma} \approx -2\sqrt{2}S_{\Pi_1} (S_{\Pi_0} + S_{\Pi_2})/J. \quad (17)$$

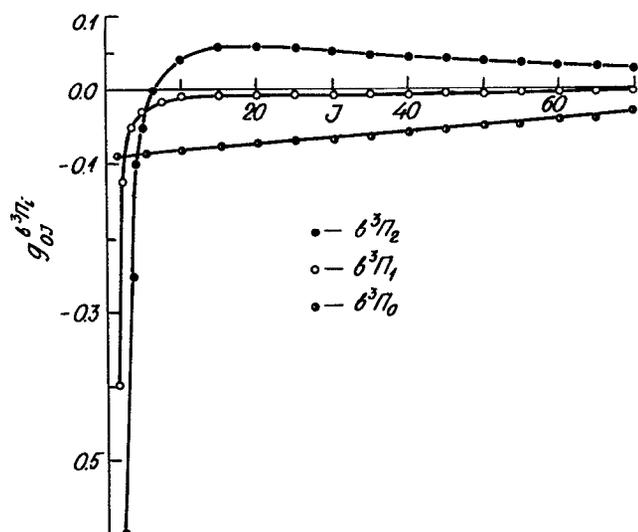


FIG. 7. The Landé factors' variation with the rotational quantum number J for the ${}^3\Pi_i$ components of nonperturbed Na₂ ($b^3\Pi_u$) triplet state with $v = 0$.

We wish to draw attention to the following peculiarity of ${}^1\Sigma^-3\Pi$ interaction effect on the magnetic properties of the ${}^1\Sigma$ state. As mentioned above, for pure Hund's case a, non-zero matrix elements exist only between the ${}^1\Sigma$ state and the ${}^3\Pi_0$ component, which is itself diamagnetic, like the ${}^1\Sigma$ state ($\Omega = 0$). It follows that this component cannot contribute towards the magnetic moments of the ${}^1\Sigma$ state. The magnetism of the latter is, in this case, determined by indirect interaction with the paramagnetic ${}^3\Pi_1$ and ${}^3\Pi_2$ components through ${}^3\Pi_0$. This effect is analogous to well known phenomenon of accidental predissociation.³⁸ It is interesting to note that the degree of interaction of the ${}^3\Pi_1$ and ${}^3\Pi_2$ components with the ${}^1\Sigma$ state increases with increasing rotational quantum number J , cf. Eq. (16a). On the other hand, the rotational magnetic moment of a molecule is well known to decrease with increasing rotation.^{10,32,38} The resulting magnetic moment is thus determined by the competition between these two processes.

We now consider specific results for the Na₂ molecule. As may be seen from Fig. 6, the potential curves of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states of Na₂ intersect and are strongly displaced with respect to each other. It follows that interaction between them is of distinctly local nature. Accordingly, the Landé factors of these states ought to depend strongly not only on rotational quantum numbers (J), but also on vibrational ones (v) in these regions. All vibrational levels of the $A^1\Sigma_u^+$ state are known to be perturbed by at least one, more frequently by two, and sometimes, within the observed J range, even by three levels of the $b^3\Pi_u$ state.^{4,7,8} In each of these regions there are three resonances corresponding to maximum interaction with components ${}^3\Pi_2$, ${}^3\Pi_1$, and ${}^3\Pi_0$, respectively, as shown in Fig. 8. In order to study the peculiarities of the behavior of the g factors of perturbed $A^1\Sigma_u^+$ and all components of $b^3\Pi_u$ states ($i = 0, 1, 2$), as well as for analysis of their dependence on the absolute value of J and on the sign of the overlap integral $\langle v_A | v_B \rangle$, cf. Eq. (15a), a

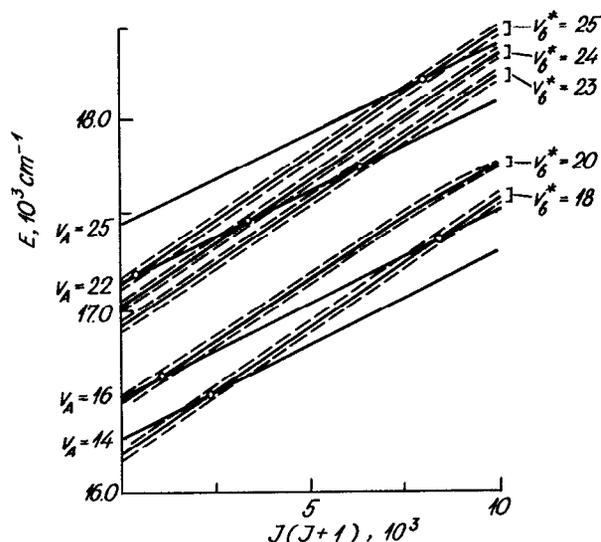


FIG. 8. Intersection of rovibronic levels Na₂ ($A^1\Sigma_u^+, v_A, J$) and Na₂ ($b^3\Pi_u, v_B^*, J$) for vibration states involved in this work. The values of triplet splitting for $b^3\Pi_u$ state (dashed lines) are strongly exaggerated.

number of vibrational levels of the $A^1\Sigma_u^+$ state were selected, having various ranges of J values, cf. Fig. 9. The g -factor values for these levels were calculated according to formula (16a), assuming $\eta_{ei} = 0$, cf. Eq. (16b). To this purpose, at first the full wave functions were found through numerical diagonalization of the 4×4 Hamilton matrix, cf. Eq. (14). The matrix elements were given in the form proposed in Ref. 7. The vibrational wave functions of the interacting states used in the calculations of $\langle v_A | v_B \rangle$, cf. Eq. (15a) were found from a numerical solution of the radial Schrödinger equation with RKR potentials for the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states over deperturbed molecular states, according to Ref. 3 and 7, respectively. The electronic matrix element ξ_{ei} was assumed to be independent of the internuclear distance.

It was found that in the vicinity of the points of intersection, i.e., in the vicinity of resonances, as shown in Fig. 8, the values and signs of mixing coefficients, i.e., of the Landé factors as well, are strongly dependent on the accuracy of the employed matrix elements of the Hamiltonian matrix, and are determined by the accuracy of the vibrational and rotational molecular constants for the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states. However, the reliability of the deperturbed molecular constants for both states, as given in the literature, is regrettably small, the constants of centrifugal distortion D_v , H_v , etc., being particularly poorly known (in percent). This, in its turn, dramatically affects the accuracy of the calculated g factors at large J values. We therefore used effective sets of molecular constants and matrix elements in the Hamiltonian matrix for more accurate calculation of full wave functions of these levels. These sets are valid only within a limited range of values of v_A , v_B , and J .^{4,7,8} The results of calculations of the rovibronic levels of the $A^1\Sigma_u^+$ state, for which the Landé factors have been measured in the present work (cf. Sec. II) are given in Table I in form of mixing coeffi-

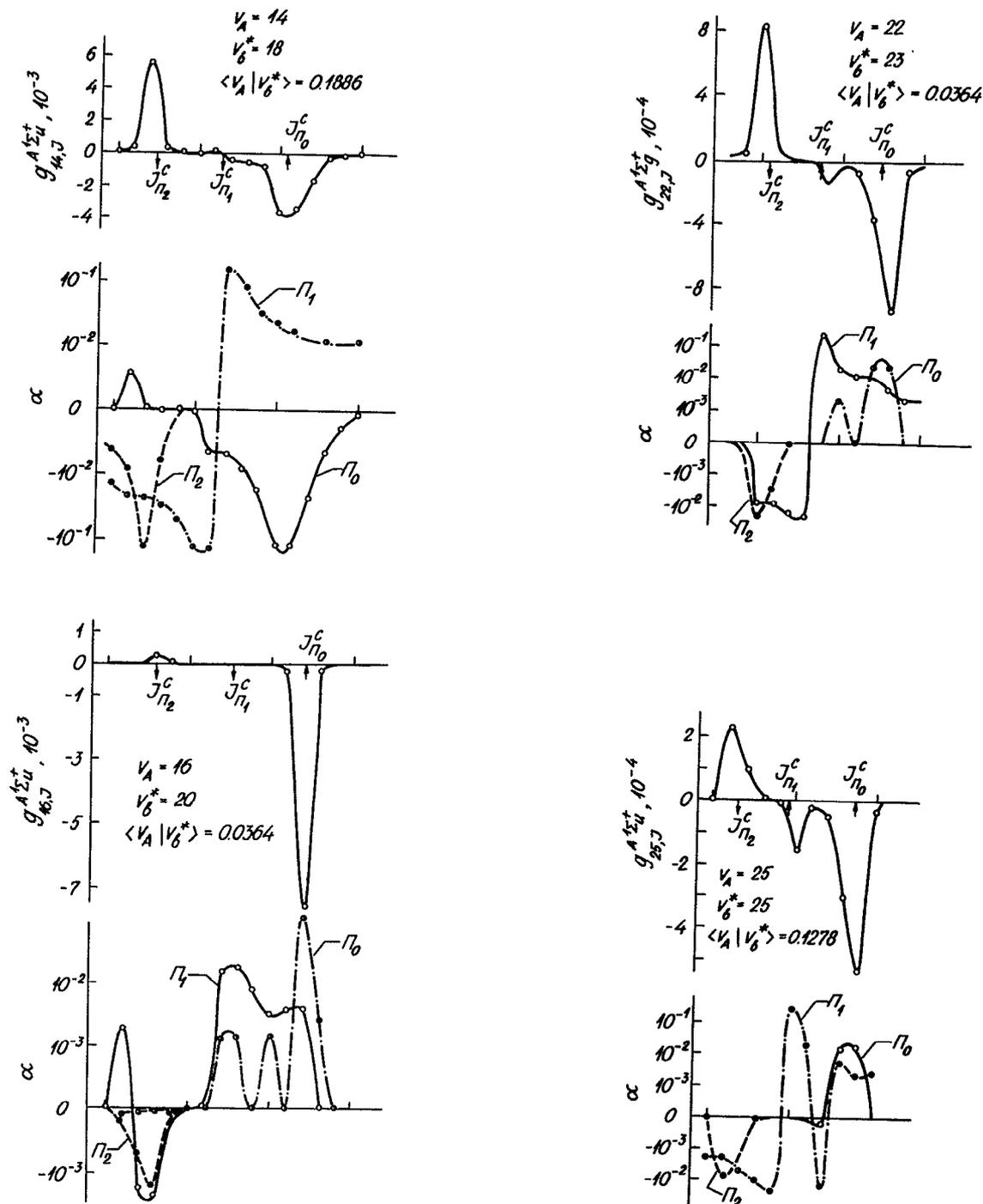


FIG. 9. J dependence of $g_{uv}^{A^1\Sigma_u^+}$ factors for $A^1\Sigma_u^+$ state, as well as of coefficients $\alpha = (g - g^*)/g$ for the components of $b^3\Pi_u$ state. Mutual $b^3\Pi_u - A^1\Sigma_u^+$ perturbation is considered according to Eq. (4). Ranges of J are 45–60 for $v_A = 14$, 25–40 for $v_A = 16$, 80–90 for $v_A = 22$, and 85–95 for $v_A = 25$.

icients and g factors. It may be seen from the presented data that level $v_A = 16$, $J = 17$ may be considered as nonperturbed with respect to other levels, i.e., its magnetism is not determined by $A^1\Sigma_u^+ - b^3\Pi_u$ interaction.

On the whole, the following conclusions can be drawn from the results of our calculations of Landé factor dependences and of mixing factors, as dependent on quantum number J values, and presented in Fig. 9:

(i) As expected, the g factors $g_{uv}^{A^1\Sigma_u^+}$ of the $A^1\Sigma_u^+$ state change relatively considerably more than the g factors of the $b^3\Pi_u$ state. Maximum changes of the values of $g_{uv}^{A^1\Sigma_u^+}$ are observed in the vicinity of intersection with the $^3\Pi_2$ component (positive sign of the g factor), and with the $^3\Pi_0$ component (negative sign of the g factor). Absence of or very insignificant resonance in the vicinity of intersection with the $^3\Pi_1$

component may be due to opposite signs of mixing coefficients for S_{Π_0} and S_{Π_2} , cf. Eq. (17).

(ii) The absolute value of $g_{vJ}^{A^1\Sigma_u^+}$ near the resonances for the given vibrational level v decreases monotonically with increasing rotational quantum number J , assuming values from 10^{-1} – 10^{-2} for low J values, down to 10^{-3} – 10^{-4} for high ones. This is due to the fact that follows from Eq. (17): the mixing coefficient values in resonance vicinity depend only weakly on absolute J value and are mainly determined by the distance between deperturbed rovibronic levels of $A^1\Sigma_u^+$ and $b^3\Pi_i$ states near the resonances.

(iii) The nature of the J dependence of g factors of perturbed $b^3\Pi_i$ states in the vicinity of resonances is affected by circumstances: first, the distance between nonperturbed rovibronic levels of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states, and second, the steepness of the J dependence of nonperturbed components of the $b^3\Pi_u$ state, cf. Fig. 7. [For sake of convenience relative additions to the nonperturbed g factors in form of $\alpha = (g^* - g)/g$ are presented in Fig. 9.] It is for both these reasons, as may be seen from Fig. 9, that the relative addition to the g factor of $b^3\Pi_i$ state is most drastically dependent on J .

C. Effect of $^1\Sigma$ – $^1\Pi$ interaction of the $A^1\Sigma_u^+$ and $B^1\Pi_u$ state Landè factors. Connection between Landè factors and Λ -doubling constants

The singlet $^1\Pi$ and $^1\Sigma$ states of diatomic molecules of similar parity ($u \leftrightarrow u$ and $g \leftrightarrow g$) interact owing to nonzero matrix elements of operator $[-1/(2\mu R^2)] \times (J^+L^- + J^-L^+)$. In energy characteristics this leads to Λ doubling of the $^1\Pi$ state, which manifests itself experimentally in the splitting of the $^1\Pi$ state levels with different parity ($+ \leftrightarrow +$ or $- \leftrightarrow -$). The Λ -doubling constant (q) is determined by the dependence³⁸

$$q_{vJ} = 2 \sum_{v^*} \langle v_J^* | L^+(R)/R^2 | v_J \rangle^2 / \Delta T_{v^*vJ}, \quad (18a)$$

where

$$L^+(R) = \langle ^1\Pi | L^+ | ^1\Sigma \rangle, \quad (18b)$$

$$\Delta T_{v^*vJ} = E_{vJ} - E_{v^*J}. \quad (18c)$$

In the case of the $^1\Sigma$ state this interaction leads to a change in the value of the experimentally found rotational constant $B_v^{\text{eff}} = B_v^{\text{true}} + q_v$. An experimental determination of the divergence of the effective rotational constant B_v^{eff} from the value B_v^{true} is difficult in the case of regular perturbations, by virtue of the smallness of q_v and its smooth dependence on the vibrational quantum number. Here B_v^{true} must be considered as the so-called “deperturbed” value of the rotational constant.³⁸

The given interaction is also known to lead to a change in the Landè factors of the states under discussion³²

$$g_{vJ} = -2 \sum_{v^*} \langle v_J^* | L^+(R)/R^2 | v_J \rangle \times \langle v_J^* | L^+(R) | v_J \rangle / \Delta T_{v^*vJ}. \quad (19)$$

As may be seen, using expressions (18a) and (19) for calcu-

lating g and q factors it is necessary to perform the summing (integrating) over all vibrational states of both the discrete and the continuous spectrum. The difficulty here is due to the necessity of executing a numerical solution of the radial Schrödinger equation for a large (in the general case, an infinite) number of levels of the discrete spectrum (v_J^*) and the continuous spectrum (ϵ_J), in order to satisfy the well known sum rule

$$\sum_{v^*} \langle v_J | v_J^* \rangle^2 + \int_{\epsilon_J} \langle v_J | \epsilon_J \rangle^2 d\epsilon_J = 1. \quad (20)$$

This problem becomes particularly acute in the case where the potential curves of the interacting electronic states are strongly displaced with respect to each other. Then condition (20) is approximately satisfied only in case of a very large number of terms in the summation and integration process in Eqs. (18a) and (19). We have used simple expressions for estimating effects of distant electronic states on q and the g factor without performing the summation and the integration over the nonbounded rovibronic levels of the perturbing state (cf. the Appendix). These expressions prove to be extremely time and labor saving in calculations.

Since there is one cause leading both to Λ doubling of rotational levels as well as to change in Landè factors, there must obviously exist a connection between the constants characterizing both effects. If such a connection is found, it becomes possible to estimate the effect of remote electronic states by means of experimentally accessible magnitudes. Hence, in order to assess such an effect in the case of interacting $A^1\Sigma_u^+$ and $B^1\Pi_u$ states of Na₂, let us start by finding in a general form the connection between q and the g factors of the interacting singlet states.

If we assume that for $^1\Pi$ and $^1\Sigma$ states $L^+(R) \approx |L^+| = \text{const}$ and $\Delta T_{v^*vJ} \approx \Delta T_e = \text{const}$, Eqs. (18a) and (19) can be written in following form:

$$q_{v^*}^{1\Pi} \approx 2 |L^+|^2 (B_{v^*}^{1\Pi})^2 / \Delta T_e, \quad (21a)$$

$$g_{v^*}^{1\Sigma} \approx -2 |L^+|^2 B_{v^*}^{1\Sigma} / \Delta T_e. \quad (21b)$$

Then, using Eqs. (21), we can easily find the connection between Λ -doubling constant of the $^1\Pi$ state and Landè factor of the $^1\Sigma$ state

$$g_{v^*}^{1\Sigma} \approx -q_{v^*}^{1\Pi} B_{v^*}^{1\Sigma} / (B_{v^*}^{1\Pi})^2. \quad (22)$$

The interaction between the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states of Na₂ is known to have been experimentally established in the course of studying the Λ doubling of the rotational levels of the $B^1\Pi_u$ state.³⁹ In order to estimate the effect of this interaction on the Landè factors of the $A^1\Sigma_u^+$ state, we employed expressions (18a) and (19), as well as approximate relations (A9) and (A10). Before we did this, however, we checked the feasibility of Eqs. (A6) and (A7) for the states where relation (20) is valid, i.e., $0 < v < 10$ and $0 < v^* < 10$. In order to simplify the calculations we assumed that $|L^+| = 1$. Calculation results for q and g factors obtained with the aid of formula (18a), Eqs. (19), (A9), and (A10) were compared for above-mentioned v values, as well as for those used in the experiment. In all cases the relative difference of the results given by Eqs. (18a), (19), (A9), and (A10) does not exceed

$\sim 2 \times 10^{-4}$, which lies far below experimental error range.

In order to construct the potential curve for the $B^1\Pi_u$ state we used data according to Refs. 39–41. Subsequently, formula (A9) was employed under the assumption $L^+(R) = \text{const}$ for calculating the values of factors q_{v^*J} for the levels of the $B^1\Pi_u$ state, viz. for $0 < v^* < 30$ and $0 < J < 100$. A comparison between experimental values of Λ -doubling constants, $q_{v^*J}^{\text{exp}}$ as presented in Ref. 39, and theoretical $q_{v^*J}^{\text{th}}$ ones shows that the magnitude $|L^+|$ can be considered as constant for all levels under study with 5% accuracy: $|L^+| = 1.42 \pm 0.05$. This demonstrates, on the one hand, the validity of the assumption $L^+(R) = \text{const}$ for the states under consideration, and confirms, on the other hand, with respect to these states, the hypothesis of pure Van Vleck precession:⁴² $\langle {}^1\Pi | L^+ | {}^1\Sigma \rangle = \sqrt{l(l+1)} = \sqrt{2}$. After that, using $|L^+|$, as obtained by means of formulas (A9) and (A10) the values of the q factors for the $B^1\Pi_u$ state were evaluated, as well as the g factor of the $A^1\Sigma_u^+$ state. The dependences of the values obtained for the vibrational (v) and rotational (J) quantum numbers are presented in Fig. 10.

Thus the interaction between the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states leads to the production of a negative magnetic moment of the order of 7.5×10^{-5} in the $A^1\Sigma_u^+$ state, which only slightly depends on v and J .

D. Effect of indirect $A^1\Sigma_u^+ - b^3\Pi_u - a^3\Sigma_u^+$ interaction on the Landé factors of the $A^1\Sigma_u^+$ state

As may be seen from Fig. 6, the next nearest to $A^1\Sigma_u^+$ paramagnetic state after $b^3\Pi_u$ and $B^1\Pi_u$ is the weakly bonded $a^3\Sigma_u^+$ state.^{43,44} Interaction with the latter can also contribute towards the rotational magnetic moment of the $A^1\Sigma_u^+$ state. The peculiarity of this interaction consists in the circumstance that it is of indirect nature, since any non-zero matrix elements between the ${}^1\Sigma_u^+$ and the ${}^3\Sigma_u^+$ state do not exist, subject to pure Hund's case a.³⁵ This interaction therefore takes place through the $b^3\Pi_0$ component of the $b^3\Pi_u$ state. Another important feature of this $A-b-a$ interactions is due to the repulsive nature of the potential curve of the $a^3\Sigma_u^+$ state in the relevant region of internuclear distances (Fig. 6). It may be of interest to note that in the case of the Li₂ molecule the potential curves of the $a^3\Sigma_u^+$ and $b^3\Pi_u$ states intersect,⁴⁵ and the interaction produces an effect of indirect predissociation.⁴⁶ Such an effect may take place also in the case of Na₂, but only for very high vibrational quantum numbers of the $A^1\Sigma_u^+$ state.⁴³ In the case of the rovibronic levels of the $A^1\Sigma_u^+$ state under consideration interaction between the $b^3\Pi_0^+$ and $a^3\Sigma_1^+$ levels is small and is of regular nature owing to the remoteness of the $a^3\Sigma_u^+$ state [$\Delta T_e = T_e(b^3\Pi_u) - T_e(a^3\Sigma_u^+) \approx 7000 \text{ cm}^{-1}$]. Nevertheless, by virtue of locality of $A^1\Sigma_u^+ - b^3\Pi_0$ interaction, the total effect of $a^3\Sigma_u^+$ on the magnetism of the $A^1\Sigma_u^+$ state is also of local nature. Using the expression for the matrix elements of ${}^3\Pi_0^+ - {}^3\Sigma_1^+$ interaction,³⁵ viz.,

$$H_{110\Sigma_1} = \langle v_b | \beta(R) / R^2 | v_a^* \rangle \sqrt{J(J+1)}, \quad (23a)$$

where

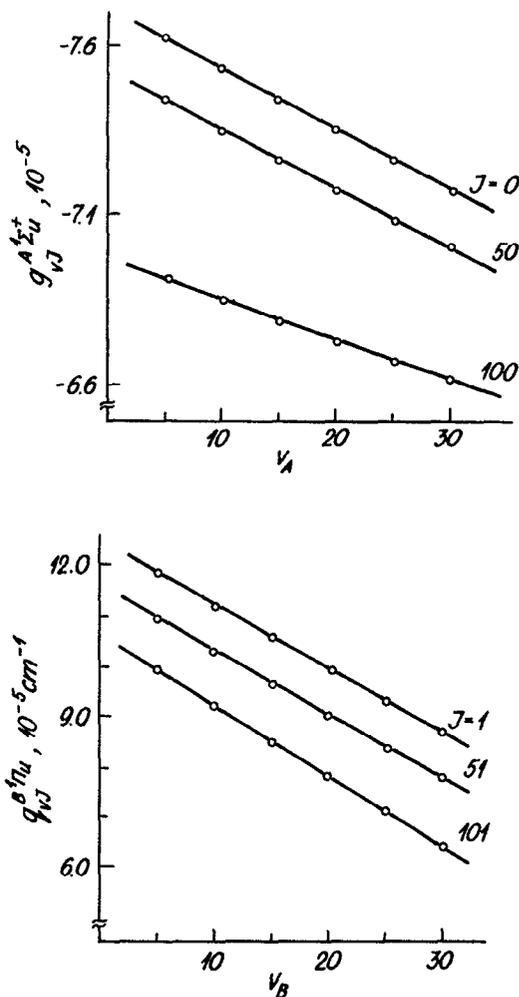


FIG. 10. v dependence of g_{vJ}^A for $A^1\Sigma_u^+$ and q_{vJ} factors for $B^1\Pi_u$ states of Na₂ as calculated according to Eqs. (A9) and (A10) for various J .

$$\beta(R) = \langle {}^3\Sigma_1^+ | L^+ | {}^3\Pi_0 \rangle, \quad (23b)$$

we obtain in first-order perturbation theory an expression for the contribution of the $a^3\Sigma_u^+$ state to the g factor of the $A^1\Sigma_u^+$ state

$$g_{vJ}^{A^1\Sigma} = 2S_{\Pi_0} \sum_{v^*} [\langle v_b | \beta(R) / R^2 | v_a^* \rangle \times \langle v_a^* | \beta(R) | v_b \rangle] / (E_{v_b} - E_{v_a^*}). \quad (24)$$

It ought to be stressed that, owing to the almost repulsive nature of the $a^3\Sigma_u^+$ state, it is necessary to perform the integration over the non-bonded states of the continuous spectrum [cf. Eq. (A1)].

Expression (24) can be easily simplified on assuming that Eq. (A2) is valid in the case of the states under discussion. Then we can use the approximate dependence (A10), thus obtaining

$$g_{vJ}^{A^1\Sigma} \approx 2S_{\Pi_0} \langle v_b | \beta^2(R) / [R^2 \Delta U(R)] | v_b \rangle, \quad (25a)$$

where (cf. Fig. 11)

$$\Delta U(R) = U_b(R) - U_a(R). \quad (25b)$$

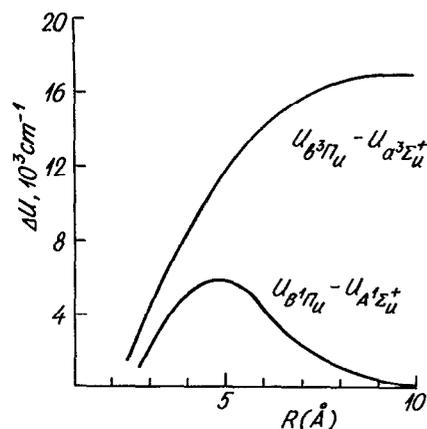


FIG. 11. The difference potential $\Delta U(R)$ between $B^1\Pi_u - A^1\Sigma_u^+$ and $b^3\Pi_u - a^3\Sigma_u^+$ states of Na₂.

Assuming further that the $b^3\Pi_u$ and $a^3\Sigma_u^+$ states, as well as the $A^1\Sigma_u^+$ and the $B^1\Pi_u$ states follow the Van Vleck “pure precession” hypothesis,⁴² the magnitude $\beta(R)$ can be estimated as $\beta(R) \approx \text{const} = 2$. We then obtain a rough assessment of the contribution of the $a^3\Sigma_u^+$ state

$$g_{\omega}^{A^1\Sigma_u^+} \approx 4S_{\Pi_0} B_v^{b^3\Pi_u} / \Delta T_e. \quad (26)$$

The contribution of the $a^3\Sigma_u^+$ state into the g factor of the $A^1\Sigma_u^+$ state as evaluated according to Eq. (26) does not exceed 0.01–0.1 of the contribution from the $b^3\Pi_u$ state. From our point of view it is small enough to neglect this effect for the vibrational levels under consideration. However, the influence of the $a^3\Sigma_u^+$ state may increase dramatically in the vicinity of intersection of the curves of the $b^3\Pi_u$ and $a^3\Sigma_u^+$ states when $[\Delta U(R)]^{-1} \rightarrow \infty$. In this situation expression (24) clearly ceases to apply, and the $b^3\Pi_u - a^3\Sigma_u^+$ perturbation changes from regular to local, such as in the case of $A^1\Sigma_u^+ - b^3\Pi_u$ mixing.

IV. DISCUSSION

The resulting g -factor values, as obtained for Na₂ ($A^1\Sigma_u^+$) from measurements ($g_{v',J'}^{\text{exp}}$) and from calculations ($g_{v',J'}^{\text{th}}$) presented in Table I are, in principle, not in contradiction to each other. The best coincidence, for $v' = 16$, $J' = 17$, might be due to the circumstance that, in this case, the contribution from $A^1\Sigma_u^+ - b^3\Pi_u$ interaction is negligibly small. On the other hand, inaccuracy in the calculation of this interaction can affect most strongly the relative error in $g_{v',J'}^{\text{th}}$ (tot) in a situation when the g -factor value (or, rather, its electronic part $g_{v',J'}^e$) is the difference of two partial contributions of interactions with the states $b^3\Pi_u$ and $B^1\Pi_u$, these contributions being comparable in value, but opposite in sign. This may be the cause of the deviation from the experimental results for levels with $v' = 14$, and $v' = 25$.

We performed an analysis, in order to elucidate the accuracy of calculations of the contribution of the $b^3\Pi_u - A^1\Sigma_u^+$ interaction to the Landè factor value of the $A^1\Sigma_u^+$ state. We found this contribution to be highly sensi-

tive to the accuracy of the unperturbed molecular constants used. This was most striking at high J values. Thus, for example, a change in the constant of centrifugal distortion D_{v^*} , for $v^* = 25$ of the $b^3\Pi_u$ level by 20% (which lies far below the experimental error in its determination) causes a change in Landè factor values of the $v' = 25$ level of the $A^1\Sigma_u^+$ state in the resonance region ($85 \leq J < 95$) by several orders of magnitude. It may be expected that systematic high precision measurements of g factors of the $A^1\Sigma_u^+$ state for each J value within the probable resonance range might permit, by solving the reverse problem, readjust the position of the rotational number of the points of intersection (cf. Figs. 8 and 9), and thus obtain more accurate values of the molecular constants.

Owing to the circumstance that the discussed electronic states of Na₂ are, in our opinion, subject to pure Hund's case a, the interference term in Eq. (16a), which corresponds to direct interaction, turns out to be negligibly small. It is known, however, that with increasing nuclear charge in the molecular series K₂, Rb₂, and Cs₂ (Ref. 47), an increase in relativistic effects takes place. In particular, the value of spin-orbit interaction becomes larger,¹³ and it is not excluded that the interference term in Eq. (16a) may play some role in the formation of the Landè factors of the state, particularly for the levels with high J values.

Moreover, with increase in spin splitting of the triplet one may apparently neglect the effect of $A^1\Sigma_u^+$ interaction with the components of $b^3\Pi_0$ and $b^3\Pi_2$ on the g factors of the $A^1\Sigma_u^+$ state. It will be the direct interaction between $A^1\Sigma_u^+$ and the $b^3\Pi_1^+$ component of $b^3\Pi_u$, which will play the main part in the formation of the nonzero magnetic moment of the A state. Expression (16a) will then assume the form

$$g_{\omega}^{A^1\Sigma_u^+} = \frac{2S_{\Sigma} S_{\Pi_1} \eta_{el} \langle v_{\Sigma} | v_{\Pi_1}^* \rangle}{\sqrt{J(J+1)}} + \frac{S_{\Pi_1}^2}{J(J+1)}, \quad (27a)$$

where

$$\eta_{el} = \langle ^1\Sigma^+ | J_a^+ | ^3\Pi_1^+ \rangle. \quad (27b)$$

The present example of $A^1\Sigma_u^+ - B^1\Pi_u$ interaction permits one to draw an interesting conclusion on how it is possible to study experimentally the characteristics of a distant electronic state. As may be seen, the effect of distant electronic states on the position of rovibronic levels of the $^1\Sigma$ state are practically impossible to observe experimentally by virtue of the insignificance of q_v with respect to the deperturbed $B_{v'}^{\text{true}}$ values. At the same time this effect can be easily assessed experimentally from the change in Landè factor value, since this change is very considerable against the zero value g factor of the unperturbed $A^1\Sigma_u^+$ state. In opposition to this, it appears to be experimentally simpler to notice and measure the Λ -doubling effect in the $^1\Pi$ state, since the change in Landè factor value can be experimentally noticed only at very large J values, when the intrinsic magnetism of the $^1\Pi$ state $g_J = -1/[J(J+1)]$ is negligible. The connection between q and the g factors, as employed in the present work, makes it possible to establish an unequivocal connection between the results of physical experiments which are alien to each other. This circumstance acts in addition to the

previously established⁴⁸ connection between g factors and constants of hyperfine (spin-orbital) interaction. Thus results of magnetism studies may in certain cases be used for the determination of structural parameters of molecules more accurately than possible by direct measurements.

Study of the effect of the above-mentioned interactions on magnetic properties appears to be of interest also from the point of view of studies of the peculiarities of their manifestations in states belonging to various cases of Hund coupling in the Li₂ → Cs₂ sequence. Thus, for example, in the case of the Li₂ molecule the peculiarity of the effect of the interactions under discussion is connected with the circumstance that for such a light molecule the value of spin-orbital interaction is lower by an order of magnitude than in the case of Na₂, leading to a Hund's case b.⁴⁷ Apparently, this leads both to considerable weakening of $A^1\Sigma_u^+ - b^3\Pi_u$ interaction effect on the magnetic properties of the $A^1\Sigma_u^+$ state and narrowing of the resonance signal's (in $g_w^{A^1\Sigma_u^+}$) dependence on J . Recently the magnetism in Li₂ ($A^1\Sigma_u^+$) was studied in Ref. 49 using the Faraday rotation method. On the other hand, with diminishing reduced mass value of the molecule an increase in the contribution of nuclear rotation takes place, cf. Eq. (13), as well as of the electronic contribution on the part of the distant $B^1\Pi_u$ state, cf. Eq. (3). Another peculiarity in the behavior of Li₂ is connected with the fact that, owing to mutual intersection of the potential curves of $b^3\Pi_u$ and $a^3\Sigma_u^+$, there is a noticeable increase in the effect of the $a^3\Sigma_u^+$ state (in comparison with Na₂), this effect necessarily being of pronounced local nature. As a further consequence of this intersection there must be a diminution in the lifetime of the perturbed levels of the $A^1\Sigma_u^+$ state, caused by accidental predissociation.⁴⁶

V. CONCLUSION

The approach used in the present work for studying perturbations, based on Landè factor measurements of perturbed diamagnetic ($\Omega = 0$) states, appears to us to be a highly competitive method permitting detailed investigation not only of local, but also of weak regular perturbations, the analysis of which may be inaccessible by traditional high-resolution spectroscopic methods.

$$\langle v_J | f(R) / \Delta U(R) | v_J^* \rangle \approx \frac{\langle v_J | f(R) | v_J^* \rangle - y_1 f'(R_c) X_2 + f(R_c) [X_2 (y_1^2 - y_2) - Y_2 y_2]}{E_{vJ} - E_{v^*J}}, \quad (A6)$$

where $X_2 = \langle v_J | (\Delta R)^2 | v_J^* \rangle$. Then multiplying both parts of Eq. (A6) with $\langle v_J^* | \mu(R) | v_J \rangle$ and using the sum rule (20) it is possible to get the approximation (A2) and also to estimate its relative error ξ_F as

$$\xi_F \approx \sum_{v^*} \{ [(f_1 - y_1)y_1 - y_2] X_2 - y_2 Y_2 \}, \quad (A7)$$

where $f_1 = f'(R_c)/f(R_c)$. It is clear that $\xi_F = 0$ in the R -centroid approximation. In real case the ξ_F value is the

APPENDIX

In the assessment of the effect of distant electronic states on the characteristics under discussion [cf., e.g., expressions (18a) and (19)] of the given rovibronic state it is necessary to calculate the following form^{38,50}

$$F = \sum_{v^*} \frac{\langle v_J | f(R) | v_J^* \rangle \langle v_J^* | \mu(R) | v_J \rangle}{E_{vJ} - E_{v^*J}} + \int \frac{\langle v_J | f(R) | \epsilon_J \rangle \langle \epsilon_J | \mu(R) | v_J \rangle d\epsilon_J}{E_{vJ} - \epsilon_J}, \quad (A1)$$

where summation and integration is performed over all rovibronic states of the discrete and continuous spectrum, $f(R)$ and $\mu(R)$ being known continuous functions of the internuclear distance.

In the case then the perturbing electronic state is far off the perturbed one, we propose a simple form for estimating the expressions of (A1) type

$$F \approx \langle v_J | f(R) \mu(R) / \Delta U(R) | v_J \rangle, \quad (A2)$$

where $\Delta U(R)$ is a potential difference of the states under consideration. Let us consider the conditions when the approximation (A2) is valid. For this purpose let us use the expansion of $\Delta U(R)$ into a Taylor series in the vicinity of the point R_c

$$\Delta U(R) = \Delta U(R_c) + \Delta U'(R_c) \Delta R + \Delta U''(R_c) (\Delta R)^2 / 2 + \dots, \quad (A3)$$

where $\Delta R = R - R_c$, and $R_c = \langle v_J | R | v_J^* \rangle / \langle v_J | v_J^* \rangle$ is so-called R centroid.⁵¹ Then neglecting the higher powers in Eq. (A3) one can obtain

$$\frac{f(R)}{\Delta U(R)} \approx \frac{f(R)}{\Delta U(R_c)} [1 - y_1 \Delta R + (y_1^2 - y_2) (\Delta R)^2], \quad (A4)$$

where $y_1 = \Delta U'(R_c) / \Delta U(R_c)$, $y_2 = \Delta U''(R_c) / [2\Delta U(R_c)]$. Taking into account that⁵²

$$E_{vJ} - E_{v^*J} = \langle v_J | \Delta U(R) | v_J^* \rangle / \langle v_J | v_J^* \rangle \approx \Delta U(R_c) (1 + y_2 Y_2 + \dots), \quad (A5)$$

where $Y_2 = \langle v_J | (\Delta R)^2 | v_J^* \rangle / \langle v_J | v_J^* \rangle$, and assuming that $f(R) \approx f(R_c) + f'(R_c) \Delta R$ is weakly dependent on R after integrating the both parts of Eq. (A4) we can obtain

smaller, the larger is the distance $\Delta U(R)$ between the interacting electronic states, and the closer to each other are the shapes of their potential curves, i.e., the smaller the difference between their vibrational and rotational constants. The $\Delta U = U_{111} - U_{12}$ and $\Delta U = U_{b^3\Pi} - U_{a^3\Sigma}$ values, as dependent on internuclear distance R are represented in Fig. 11 for the electronic states discussed in this paper. Additionally, the ξ_F is smaller for the low vibrational levels and for the states with small values of the parameter $\gamma = B_e / \omega_e$.⁵³ It may be of interest to know that the obtained expression

(A2) is similar to the approximation for lifetime estimation⁵⁴

$$\tau_{\omega}^{-1} \approx \langle v_J | [\Delta U(R)]^3 \mu^2(R) | v_J \rangle. \quad (\text{A8})$$

Thus substituting $f(R) = L^+(R)/R^2$, $\mu(R) = L^+(R)$ into Eq. (A2), we obtain the following expressions for the g and τ factors:

$$g_{v^*J} \approx 2 \langle v_J^* | [L^+(R)]^2 / [R^4 \Delta U(R)] | v_J^* \rangle, \quad (\text{A9})$$

$$g_{\omega} \approx -2 \langle v_J | [L^+(R)]^2 / [R^2 \Delta U(R)] | v_J \rangle. \quad (\text{A10})$$

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