

On the determination of absolute intensities of rovibrational lines for XY₂-type molecules of C_{2v} symmetry group

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Matrix elements of the effective dipole moment operator are determined for the XY₂ molecules of C_{2v} symmetry group. Contributions from rotational operators proportional to J_α operators to the third power are taken into account.

Solution of almost any problem of atmospheric optics requires, to that or other degree, knowledge of the precision with which quantitative characteristics of absorption spectra of atmospheric gases and pollutants are known. This information, in its turn, can be obtained from high-accuracy calculations of the parameters (positions and intensities) of rovibrational spectral lines of the corresponding molecules. In recent years, because of the considerable progress achieved in the experimental technology (in particular, appearance of high-accuracy laser spectrometers and Fourier transform spectrometers), the measurement accuracy in intensity of isolated rovibrational lines has been increased by orders of magnitude. This fact necessitates improvement and modification of theoretical equations used for description of molecular spectra with the allowance for finer, than earlier, effects. This paper is just devoted to such a refinement of equations describing the intensities of rovibrational lines of XY₂ molecules of C_{2v} symmetry group (this class of molecules includes, in particular, water vapor H₂O).

The general equation for the intensity of a rovibrational line (see, for example, Ref. 1) has the following form:

$$k_{\sigma} = \frac{8\pi^3\sigma}{4\pi\epsilon_0 3hc} \left[1 - \exp\left(-\frac{hc\sigma}{kT}\right) \right] \times \\ \times N \frac{g_A}{Z(T)} \exp\left(-\frac{E_A}{kT}\right) \sum_a \sum_b 3 |\langle a | \mu_z | b \rangle|^2. \quad (1)$$

In Eq. (1), T and N are, respectively, the medium temperature and the number of gas molecules in a unit volume (the latter can be related to pressure); σ and E_A are the transition frequency and the energy of the lower quantum state that are assumed known from solution of the Schrödinger equation for a free molecule; g_A and $Z(T)$ are the statistical weight and the partition function¹ that are also assumed known. Thus, the main problem is calculation of matrix elements of the dipole moment operator $\langle a | \mu_z | b \rangle$.

It should be noted that rigorous solution of this problem, that is, calculation of the matrix elements $\langle a | \mu_z | b \rangle$, is impossible, because there is no exact solution to the Schrödinger equation with the rotational-vibrational molecular Hamiltonian. Therefore, some approximate methods are applied in molecular spectroscopy. One of such methods is the method of effective operators^{2,3} based on the operator perturbation theory. This method allows correct description of some or other groups of rotation-vibration states and quantum transitions. It can be shown¹ that within the framework of this method the matrix element $\langle a | \mu_z | b \rangle$ of the dipole moment operator (now the effective dipole moment operator describing transitions between any rotational states of a selected pair of vibrational states or groups of resonant vibrational states) should have the following form:

$$R_a^b = \langle a | \mu_z | b \rangle = \\ = \sum_{V \in A} \sum_{V' \in BKK'} C_{JK\Gamma}^V * C_{J'K'\Gamma'}^{V'} \langle JK\Gamma |^{VV'} \mu_z | J'K'\Gamma' \rangle, \quad (2)$$

where $\sum_{V \in A} \sum_K C_{JK\Gamma}^V |JK\Gamma\rangle$ are the eigenfunctions of one group of resonant rotation-vibration states (for example, the initial states of the transition), $\sum_{V' \in BKK'} C_{J'K'\Gamma'}^{V'} |J'K'\Gamma'\rangle$ are the eigenfunctions of another group (for example, the final states of the transition). Here $|JK\Gamma\rangle$ are the basis rotation-vibration functions, which are usually taken in the form of the Wang basis for asymmetric top molecules⁴:

$$|JK\Gamma\rangle = \frac{1}{\sqrt{2}} (|JK\rangle \pm |J-K\rangle), \quad (3)$$

where $|JK\rangle$ are ordinary rotational functions,⁵ and the symmetry Γ depends on the parity of the quantum number K and the sign in the right-hand side of Eq. (3); $C_{JK\Gamma}^V$ are the numerical factors that are determined from solution of the Schrödinger equation

for a free molecule, and ${}^{VV'}\mu_z$ are effective dipole moment operators connected with pairs of vibrational states $|V\rangle$ and $|V'\rangle$.

Finally, the problem of calculation of the matrix elements $\langle JK\Gamma|{}^{VV'}\mu_z|J'K'\Gamma'\rangle$ reduces to construction of the correct operator ${}^{VV'}\mu_z$ in the form of the corresponding sums of rotational operators of different order of smallness

$${}^{VV'}\mu_z = |V\rangle\langle V'| \sum_J {}^{VV'}A_j \quad (4)$$

and following the determination of matrix elements of these operators on the functions $|Jk\rangle$, where $k = \pm K$ and $-J \leq k \leq J$.

For XY_2 molecules of the C_{2v} symmetry group, whose vibrational states can have only A_1 or B_1 symmetry, the corresponding results for both the possible operators A_j proportional to the components J_α of the total angular momentum operator to the first and second power and the corresponding matrix elements were presented in Ref. 1. In this paper, we present the

corresponding results for the operators ${}^{VV'}A_j$ proportional to the operators J_α to the third power.

The question on what rotational operators contribute to ${}^{VV'}\mu_z$ depending on the symmetry of the functions $|V\rangle$ and $|V'\rangle$ can be answered most easily using the symmetry properties of a molecule. For XY_2 molecules of the C_{2v} symmetry group, the J_α operators transform as follows: $J_x \in A_2$, $J_y \in B_1$, $J_z \in B_2$. The elements of the direction cosine matrix $\varphi_\alpha = k_{z\alpha}$ (hereinafter we follow the designations of Ref. 1), in their turn, transform as $\varphi_x \in A_2$, $\varphi_y \in B_1$, $\varphi_z \in B_2$. Taking this into account, we can show that only the combinations of the J_α rotational operators to the third power that are presented in Tables 1 and 2 can contribute to the reduced dipole moment ${}^{VV'}\mu_z$.

The values of nonzero matrix elements are given in the last columns of these Tables. The designations in Tables 1 and 2 correspond to that used in Ref. 1.

Table 1. Perpendicular band

j	${}^V A_j$	n	$\langle JK {}^V A_j J + \Delta JK + n\Delta K\rangle$, $\Delta K = 0$
9	$\frac{1}{2} [\varphi_x, iJ_y J^2]_+ - \frac{1}{2} [i\varphi_y, J_x J^2]_+$	0	$0, \Delta J = 0$
			$\langle JK \varphi_z J + \Delta JK\rangle (m^2 + 1) m\Delta J$, $\Delta J = \pm 1$
10	$\frac{1}{2} [\varphi_x, iJ_y J^2]_+ + \frac{1}{2} [i\varphi_y, J_x J^2]_+$	2	$\langle JK \varphi_x JK + \Delta K\rangle \Delta K (J - 1 - K\Delta K)^{1/2} (J + 2 + K\Delta K)^{1/2} J(J + 1)$, $\Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K\rangle \Delta K m (m - 1) \times$ $\times (m - 1 - K\Delta K)^{1/2} (m + 2 + K\Delta K)^{1/2}$, $\Delta J = \pm 1$
11	$\frac{1}{2} [\varphi_x, [iJ_y, J_z^2]_+]_+ - \frac{1}{2} [i\varphi_y, [J_x, J_z^2]_+]_+$	0	$0, \Delta J = 0$
			$\langle JK \varphi_z J + \Delta JK\rangle m\Delta J (2K^2 + 1)$, $\Delta J = \pm 1$
12	$\frac{1}{2} [\varphi_x, [iJ_y, J_z^2]_+]_+ + \frac{1}{2} [i\varphi_y, [J_x, J_z^2]_+]_+$	2	$\langle JK \varphi_x JK + \Delta K\rangle \Delta K (J - 1 - K\Delta K)^{1/2} \times$ $\times (J + 2 + K\Delta K)^{1/2} [1 + 2(K + \Delta K)^2]$, $\Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K\rangle \Delta K (m - 1 - K\Delta K)^{1/2} \times$ $\times (m + 2 + K\Delta K)^{1/2} [1 + 2(K + \Delta K)^2]$, $\Delta J = \pm 1$
13	$\frac{1}{2} [\varphi_x, i(J_x J_z J_y + J_y J_z J_x)]_+$	2	$\langle JK \varphi_x JK + \Delta K\rangle \Delta K (K + \Delta K)^2 [J(J + 1) - (K + \Delta K)(K + 2\Delta K)]^{1/2}$, $\Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K\rangle (K + \Delta K) (1 + K\Delta K - m) \times$ $\times [m(m + 1) - (K + \Delta K)(K + 2\Delta K)]^{1/2}$, $\Delta J = \pm 1$
14	$\frac{1}{2} [\varphi_x, [iJ_y, J_x^2 - J_y^2]_+]_+ - \frac{1}{2} [i\varphi_y, [J_x, J_x^2 - J_y^2]_+]_+$	2	$\langle JK \varphi_x JK \pm 1\rangle (\mp 1) [J(J + 1) - K(K \pm 1)(K \pm 2)]^{1/2}$, $\Delta J = 0$
			$0, \Delta J = \pm 1$
15	$\frac{1}{2} [\varphi_x, [iJ_y, J_x^2 - J_y^2]_+]_+ + \frac{1}{2} [i\varphi_y, [J_x, J_x^2 - J_y^2]_+]_+$ 0 , if $\Delta J = 0$	0	$\langle JK \varphi_x J + \Delta JK - 1\rangle \Delta K \{8m(1 - m \pm K) - 1\}$, $\Delta J = \pm 1$
		4	$\langle JK \varphi_x JK + \Delta K\rangle \Delta K [J(J + 1) - (K + \Delta K)(K + 2\Delta K)]^{1/2} \times$ $\times [J(J + 1) - (K + 2\Delta K)(K + 3\Delta K)]^{1/2} \times$ $\times [J(J + 1) - (K + 3\Delta K)(K + 4\Delta K)]^{1/2}$, $\Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K\rangle \Delta K [m(m + 1) - (K + \Delta K)(K + 2\Delta K)]^{1/2} \times$ $\times [m(m + 1) - (K + 2\Delta K)(K + 3\Delta K)]^{1/2} \times$ $\times [m(m + 1) - (K + 3\Delta K)(K + 4\Delta K)]^{1/2}$, $\Delta J = \pm 1$

Table 2. Parallel band

j	V_{A_j}	n	$\langle JK V_{A_j} J + \Delta JK + n\Delta K \rangle, \Delta K = \pm 1$
9	$[i\varphi_y, J_z J^2]_+$	1	$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle [J(J+1)K\Delta K + (J+\Delta J)(J+\Delta J+1)(1+K\Delta K)], \Delta J = 0, \pm 1$
10	$[i\varphi_y, J_z^3]_+$	1	$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle [(1+K\Delta K)^3 + (K\Delta K)^3], \Delta J = 0, \pm 1$
11	$[\varphi_z, iJ_y J^2]_+$	1	$\langle JK \varphi_x JK + \Delta K \rangle J(J+1)(1+2K\Delta K), \Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle m [2m(K\Delta K - m) + (m-1)], \Delta J = \pm 1$
12	$[\varphi_z, [iJ_y, J_z^2]_+]_+$	1	$\langle JK \varphi_x JK + \Delta K \rangle (1+2K\Delta K) [K^2 + (K+\Delta K)^2], \Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle (1+2K\Delta K - 2m) [K^2 + (K+\Delta K)^2], \Delta J = \pm 1$
13	$[\varphi_z, [iJ_y, J_x^2 - J_y^2]_+]_+$	1	$\langle JK \varphi_x JK + \Delta K \rangle \times$ $\times [1 + 3K\Delta K + 3K^2 + 2K^3 \Delta K - (1 + 2K\Delta K) J(J+1)], \Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle [(m^2 - K^2)(2m - 2K\Delta K - 1) + (1 - m + K\Delta K)(1 + 2K\Delta K)], \Delta J = \pm 1$
		3	$\langle JK \varphi_x JK + \Delta K \rangle (3 + 2K\Delta K) [J(J+1) - (K+\Delta K)(K+2\Delta K)]^{1/2} \times$ $\times [J(J+1) - (K+\Delta K)(K+2\Delta K)]^{1/2} \times$ $\times [J(J+1) - (K+2\Delta K)(K+3\Delta K)]^{1/2}, \Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle (-2m + 2K\Delta K + 3) \times$ $\times [m(m+1) - (K+\Delta K)(K+2\Delta K)]^{1/2} \times$ $\times [m(m+1) - (K+2\Delta K)(K+3\Delta K)]^{1/2}, \Delta J = \pm 1$
14	$\frac{1}{2} [i\varphi_y, [J_z, J_x^2 - J_y^2]_+]_+ -$ $-\frac{1}{2} \{\varphi_x, [J_z, i[J_x J_y + J_y J_x]]_+\}_+$	1	$\langle JK \varphi_x JK + \Delta K \rangle \{-K\Delta K [J(J+1) - K(K-\Delta K)] -$ $-\Delta K(K+\Delta K) [J(J+1) - (K+\Delta K)(K+2\Delta K)]\}, \Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle \{K\Delta K(m - K\Delta K)(m - K\Delta K + 1) +$ $+ (K+\Delta K)\Delta K(m-1 - K\Delta K)(m-2 - K\Delta K)\}, \Delta J = \pm 1$
15	$\frac{1}{2} [i\varphi_y, [J_z, J_x^2 - J_y^2]_+]_+ +$ $+\frac{1}{2} \{\varphi_x, [J_z, i[J_x J_y + J_y J_x]]_+\}_+$	3	$\langle JK \varphi_x JK + \Delta K \rangle (3 + 2K\Delta K) [J(J+1) - (K+\Delta K)(K+2\Delta K)]^{1/2} \times$ $\times [J(J+1) - (K+2\Delta K)(K+3\Delta K)]^{1/2}, \Delta J = 0$
			$\langle JK \varphi_x J + \Delta JK + \Delta K \rangle (3 + 2K\Delta K) \times$ $\times [m(m+1) - (K+\Delta K)(K+2\Delta K)]^{1/2} \times$ $\times [m(m+1) - (K+2\Delta K)(K+3\Delta K)]^{1/2}, \Delta J = \pm 1$

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References

1. J.M. Flaud and C. Camy-Peyret, Mol. Phys. **15**, 278–310 (1975).
2. D. Papoušek and M.R. Aliev, *Molecular Vibrational-Rotational Spectra* (Academia, Prague, 1982), 323 pp.
3. Yu.S. Makushkin and O.N. Ulenikov, Izv. Vyssh. Uchebn. Zaved., Ser. Fiz., No. 3, 11–16 (1975).
4. Y.Y. Kwan, Molecular Spectroscopy **71**, No. 2, 260–280 (1978).
5. D.A. Varshalovich, A.N. Moskalev, and V.K. Khersonskii, *Quantum Theory of Angular Momentum* (Nauka, Leningrad, 1975), 439 pp.