DERIVATIVES OF THE DIPOLE MOMENT FUNCTIONS FOR ISOTOPIC SPECIES OF THE OZONE MOLECULE

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A method for studying the isotope substitution effect based on an analysis of transformations of intramolecular coordinates that allows one to establish isotopic relations between molecular constants and spectroscopic parameters has been applied to the ozone molecule. The lower-order derivatives of the dipole moment functions with respect to the normal coordinates have been calculated for all isotopic species of the ozone molecule with the help of the data on the main isotope of ozone.

Ozone is an important component of atmospheric air. It plays a significant role in the radiative balance of the Earth. By now reasonably large volume of experimental data on infrared and microwave spectra of the main isotopic species of ozone has been accumulated,[1-2] but the ozone isotopes have been covered only scarcely because of the difficulty of preparation of pure isotopes. A researcher is always forced to work with a mixture of several isotopic species. Interpretation of the spectrum of this gas mixture with lines of absorption of various isotopes is a very complicated problem, especially if we take into account high density of lines and various resonances typical of the ozone spectrum. In this connection, theoretical calculations of the parameters of spectral lines of various isotopes become urgent.

Thus, to determine an isotopically invariant surface of the dipole molecular moment, the quantum-chemical *ab initio* calculation methods are widely used. However, these methods, although providing qualitatively correct description, have insufficient accuracy to reproduce the experimental parameters.[3,4] At the same time, line intensities for vibrational-rotational transitions carry the information about the dipole moment function of the molecule whose parameters are determined by solving the inverse spectroscopic problem with the use of the experimentally measured parameters.

The method of effective operators in which the spectroscopic parameters and the molecular constants are isotopically dependent[5] is one of the widely used methods for solving direct and inverse spectroscopic problems. Its application requires the knowledge of the parameters of an individual isotopic species obtained from the data on the main isotope. Thus, to determine the individual isotopically dependent parameters, namely, the lowest-order (that is, first and second) derivatives of the dipole moment function with respect to the normal coordinates, the model of polar tensors[6]

is used developed for the description of vibrational motion of the molecule. This model was used to calculate the first derivatives of the dipole moment function of ozone isotopes in Ref. 7.

However, another method exists for studying the effect of isotopic substitution on the parameters of the effective operators.[8,9] This method is based on an analysis of transformations of intramolecular coordinates. It allows the isotopic relations to be established not only between the molecular constants, but also between the spectroscopic parameters.

In the present paper, we calculate the lowest-order derivatives of the dipole moment function with respect to the normal coordinates for all isotopic species of ozone on the basis of isotopic relations suggested within the framework of the above-mentioned approach.[8,9]

THEORY

In the Born–Oppenheimer approximation the dipole moment of a molecule P_α averaged over the electronic variables and written down in the stationary system of spatial coordinates is independent of the nuclear mass and is isotopically invariant

$$P_\alpha(R) = P'_\alpha(R), \qquad (1)$$

where $P'_\alpha(R)$ is the dipole isotope operator and R specifies the spatial coordinates.

When we proceed from the spatial coordinates R to the normal coordinates Q and angular variables that specify the system of coordinates affixed to the molecule, the relations for the dipole moment operators of the main and isotope-substituted molecules are different[9]

$$P_\alpha = \sum_\beta K_{\alpha\beta} \left\{ p_\beta^0 + \sum_i p_\beta^i Q_i + \sum_{ij} p_\beta^{ij} Q_i Q_j + ... \right\}, \qquad (2)$$

$$P'_\alpha = \sum_\beta K'_{\alpha\beta} \left\{ \mu_\beta^0 + \sum_i \mu_\beta^i Q'_i + \sum_{ij} \mu_\beta^{ij} Q'_i Q'_j + ... \right\}, \qquad (3)$$

where $K_{\alpha\beta}$ and $K'_{\alpha\beta}$ are the matrices of the directional cosines; Q_i and Q'_i are the normal dimensional coordinates; p_β^0 and μ_β^0 are the components of the constant dipole moment; and $p_\beta^{i...k}$ and $\mu_\beta^{i...k}$ are the derivatives of the dipole moment function with respect to the normal coordinates for the main species and arbitrary isotope, respectively.

The relationship between the directional cosines can be written in the following form:

$$K'_{\alpha\beta} = \sum_\gamma K_{\alpha\gamma} \varkappa_{\gamma\beta} , \qquad (4)$$

where $\varkappa_{\gamma\beta}$ is the rotation matrix that brings into coincidence the axes of the coordinate system affixed to the main species of the molecule with the axis of the coordinate system affixed to the isotopomer. The matrix $\varkappa_{\gamma\beta}$ will be a function of the normal coordinates because Eq. (4) must be valid for any instantaneous configuration of nuclei. In case of small vibrations, it can be expanded into a series in the normal coordinates[9]

$$\varkappa_{\alpha\beta}(Q') = \varkappa_{\alpha\beta}(Q) = \varkappa_{\alpha\beta}^0 + \sum_i \varkappa_{\alpha\beta}^i Q_i +$$

$$+ \sum_{ij} \varkappa_{\alpha\beta}^{ij} Q_i Q_j + ... \; . \qquad (5)$$

The relationship between the normal coordinates of two isotopes can be represented in a similar way as

$$Q_i = \sum_j \alpha_i^j Q'_j + \sum_{jl} \alpha_i^{jl} Q'_j Q'_l + ... \; . \qquad (6)$$

By equating Eqs. (1) and (2) and using Eqs. (4) − (6), the relationships can be obtained that connect the components of the permanent dipole moment and the first and second derivatives of the dipole moment function with respect to the normal coordinates of two isotopes, namely

$$\mu_\beta^0 = \sum_\gamma \varkappa_{\gamma\beta}^0 p_\gamma^0 , \qquad (7)$$

$$\mu_\beta^i = \sum_{\gamma,j} (\varkappa_{\gamma\beta}^0 p_\gamma^j + \varkappa_{\gamma\beta}^j p_\gamma^0) \, \alpha_i^j , \qquad (8)$$

$$\mu_\beta^{ij} = \sum_\gamma \left\{ \sum_l (\varkappa_{\gamma\beta}^0 p_\gamma^l + \varkappa_{\gamma\beta}^l p_\gamma^0) \, \alpha_j^{il} + \right.$$

$$\left. + \sum_{i'j'} (\varkappa_{\gamma\beta}^0 p_\gamma^{i'j'} + \varkappa_{\gamma\beta}^{i'} p_\gamma^{j'} + \varkappa_{\gamma\beta}^{i'j'} p_\gamma^0) \, \alpha_i^{i'} \alpha_j^{j'} \right\} . \qquad (9)$$

The relationships for the coefficients $\varkappa_{\alpha\beta}^0$, $\varkappa_{\alpha\beta}^j$, $\varkappa_{\alpha\beta}^{ij}$, α_i^j, and α_i^{jl} are functions of the molecular characteristics and equilibrium geometry of the ground state and are reported in Ref. 8. In this case, the matrices constructed to calculate the derivatives are dimensional, which makes the calculation of the derivatives and especially of their confidence levels more difficult. However, it can be seen that Eqs. (7)−(9) remain unchanged if we use the same line of reasoning for the dimensionless normal coordinates. In this case, the coefficients $\varkappa_{\alpha\beta}^0$, $\varkappa_{\alpha\beta}^j$, $\varkappa_{\alpha\beta}^{ij}$, α_i^j, and α_i^{jl} entering the formulas will be dimensionless. Their relationships with corresponding dimensional coefficients are given in Appendix. It should be noted that Eqs. (7)−(9) were derived in the Born−Oppenheimer approximation under assumption of small vibrations.

RESULTS AND CONCLUSIONS

Based on the data on the main isotope of ozone, the parameters of the dipole moment function were calculated by Eqs. (7)−(9). The parameters of the force field and the equilibrium configuration $^{16}O_3$ were borrowed from Ref. 7, harmonic frequencies − from Ref. 10, and the permanent dipole moment − from Ref. 1. The calculated values of the first derivatives and components of the permanent dipole moment for symmetric and nonsymmetric isotopic substitution are tabulated in Tables I and II. The results obtained by the method of polar tensors and the derivatives found from the experimental data on the line intensities are also given for comparison. The figures in the parentheses correspond to a 68% confidence level in the least significant figure for the given parameter. It is seen that all values of derivatives obtained by different methods agree well with each other.

The calculated values of the second derivatives of the dipole moment functions for isotopomers are presented in Tables III and IV. These results have been obtained for the first time and are especially topical considering practically complete lack of the experimental data on the overtone line intensities and combination frequencies. Therefore, the calculated values of the second derivatives were compared only for the isotope $^{18}O_3$.

The derivatives were calculated from the data on the parameters θ_α of the effective moment of transition $\tilde{\mu}_z^{vv'}$ for the first triad of interacting states of $^{18}O_3$ (see Ref. 19). It should be remembered that the spectroscopic parameters θ_α standing before the operator $\varphi(z_\alpha)$ make the main contribution to the line intensities and are found by solving the inverse spectroscopic problem[5]:

$$\tilde{\mu}_z^{vv'} = <v \, | \, \tilde{\mu}_z | \, v'> = \sum_\alpha \theta_\alpha \, \varphi(z_\alpha) -$$

$$- i \, / \, 2 \sum_{\alpha\beta} \theta_{\alpha,\beta} \, [\varphi_{z\alpha}, \, J_\beta]_+ - ...$$

TABLE I. *The first derivatives of the dipole moment (Debye) function. Symmetric isotopic substitution.*

Molecule	References	μ_x^1	μ_x^2	μ_z^3
$^{16}O_3$	Ref. 1	− 0.02185	− 0.06529	− 0.2662
$^{17}O_3$	Our calculations	− 0.02150 (5)	− 0.06425 (5)	− 0.26197 (5)
	Ref. 18	− 0.02145		− 0.2622
$^{18}O_3$	Our calculations	− 0.02120 (5)	− 0.06425 (5)	− 0.26197 (5)
	Ref. 7	− 0.0212	− 0.0634	− 0.2585
	Ref. 13	− 0.02087		− 0.2585
	Ref. 15		− 0.06796	
$^{16}O^{17}O^{16}O$	Our calculations	− 0.02330 (6)	− 0.06473 (6)	− 0.26365 (5)
	Ref. 16	− 0.02326		− 0.2636
$^{16}O^{18}O^{16}$	Our calculations	− 0.02466 (8)	− 0.06418 (7)	− 0.26134 (6)
	Ref. 7	− 0.0247	− 0.0642	− 0.26113
	Ref. 11	− 0.0246	− 0.0688	− 0.2614
	Ref. 14		− 0.0690	
$^{18}O^{16}O^{18}$	Our calculations	− 0.0185 (2)	− 0.0643 (1)	− 0.26327 (9)
	Ref. 7	− 0.0185	− 0.0643	− 0.2635
	Ref. 13	− 0.01938		− 0.2609
	Ref. 15		− 0.06895 (4)	

TABLE II. *Permanent dipole moment and the first derivatives of the dipole moment(Debye) function. Nonsymmetric isotopic substitution*

Parameter	$^{17}O^{17}O^{16}O$ Our calculations	$^{17}O^{16}O^{16}O$ Our calculations	$^{17}O^{16}O^{16}O$ References	$^{18}O^{16}O^{16}O$ Our calculations	$^{18}O^{16}O^{16}O$ References	$^{18}O^{18}O^{16}O$ Our calculations	$^{18}O^{18}O^{16}O$ References
μ_x^e	0.5421 (5)	0.5421 (5)		0.5425 (3)		0.5420 (5)	
μ_z^e	0.0040 (6)	0.0038 (5)		0.0072 (5)		0.008 (1)	
μ_x^1	− 0.02199 (8)	− 0.206 (1)	− 0.02134 (54) (Ref. 17)	− 0.0189 (1)	− 0.01446 (130) (Ref. 15) − 0.0189 (Ref. 7)	− 0.0216 (2)	− 0.0215 (Ref. 17)
μ_x^2	− 0.06449 (5)	− 0.06502 (5)		− 0.06489 (5)	− 0.070004 (50) (Ref. 14) − 0.0649 (Ref. 7)	− 0.06381 (7)	−0.066527 (45) (Ref. 15) − 0.0639 (Ref. 7)
μ_x^3	0.0042 (4)	0.0041 (4)		0.0071 (4)	0.0074 (Ref. 7)	0.0077 (8)	0.0080 (Ref. 7)
μ_z^1	− 0.040 (2)	− 0.043 (2)		− 0.076 (2)	0.00152 (74) (Ref. 12) − 0.0809 (Ref. 7)	− 0.070 (2)	− 0.0736 (Ref. 7)
μ_z^2	0.0019 (3)	0.0019 (3)		0.0037 (2)	0.0037 (Ref. 7)	0.0036 (6)	0.0036 Ref. 7
μ_z^3	− 0.2596 (2)	− 0.2618 (4)	− 0.2626 (31) (Ref. 17)	− 0.2535 (6)	− 0.2623 (15) (Ref. 12) − 0.2521 (Ref. 7)	− 0.2500 (6)	− 0.2492 (Ref. 7)

TABLE III. The second derivatives of the dipole moment (Debye) function. Symmetric isotopic substitution.

Parameter	$^{16}O^{16}O^{16}O$	$^{17}O^{17}O^{17}O$	$^{18}O^{18}O^{18}O$	$^{16}O^{17}O^{16}O$	$^{16}O^{18}O^{16}O$	$^{18}O^{16}O^{18}O$
μ_x^{11}	− 0.00364**	− 0.0035 (1)	− 0.00343 (9) − 0.0037 (3)*	− 0.00316 (5)	− 0.00272 (5)	− 0.0043 (1)
μ_x^{12}	0.00874**	0.0085 (1)	0.00823 (9)	0.00867 (5)	0.00859 (5)	0.0083 (1)
μ_x^{22}	− 0.00136**	− 0.0013 (1)	− 0.00128 (9)	− 0.00162 (5)	− 0.00187 (5)	− 0.0008 (1)
μ_x^{33}	0.00747**	0.0072 (1)	0.00704 (9) 0.0048 (5)*	0.00741 (5)	0.00736 (5)	0.0072 (1)
μ_z^{13}	0.0444**	0.0430 (5)	0.0418 (5) 0.0439 (5)*	0.0437 (2)	0.0430 (2)	0.0432 (5)
μ_z^{23}	0.0012**	0.0012 (3)	0.0011 (3)	0.0007 (1)	− 0.00002 (15)	0.0023 (3)

* Our calculations based on the data of Ref. 19.
** Ref. 1.

TABLE IV. The second derivatives of the dipole moment (Debye) function. Nonsymmetric isotopic substitution.

Parameter	$^{17}O^{17}O^{16}O$	$^{17}O^{16}O^{16}O$	$^{18}O^{16}O^{16}O$	$^{18}O^{18}O^{16}O$
μ_x^{11}	− 0.0032 (1)	− 0.0036 (1)	− 0.00323 (6)	− 0.0025 (1)
μ_x^{12}	0.0084 (1)	0.0085 (1)	0.00810 (5)	0.0080 (1)
μ_x^{13}	0.00141 (4)	0.00157 (8)	0.00278 (7)	0.00229 (4)
μ_x^{22}	− 0.0015 (1)	− 0.0012 (1)	− 0.00106 (5)	− 0.0015 (1)
μ_x^{23}	− 0.00134 (4)	− 0.00141 (6)	− 0.00252 (5)	− 0.00231 (6)
μ_x^{33}	0.0071 (1)	0.0071 (1)	0.00654 (6)	0.0066 (1)
μ_z^{11}	0.0130 (5)	0.0138 (7)	0.0241 (5)	0.0219 (7)
μ_z^{12}	− 0.00007 (6)	0.00003 (7)	0.00011 (6)	− 0.0002 (1)
μ_z^{13}	0.0414 (5)	0.0419 (5)	0.0369 (4)	0.0366 (6)
μ_z^{22}	− 0.00024 (2)	− 0.00024 (2)	− 0.00045 (2)	− 0.00045 (5)
μ_z^{23}	0.0009 (3)	0.0015 (3)	0.0018 (1)	0.0007 (3)
μ_z^{33}	− 0.0125 (5)	− 0.0133 (7)	− 0.0230 (5)	− 0.0208 (6)

Relationships connecting the spectroscopic parameters θ_α with the molecular ones, namely, with the derivatives of the dipole moment for the overtones and the composite frequencies, are well-known.[5] As can be seen from Table III, the values of the derivatives μ_x^{11} and μ_z^{13} obtained by two different methods agree well with each other. At the same time, the value of the derivative μ_x^{33} calculated from the isotopic relations significantly exceeds the corresponding value determined from the experimental data.

The isotopic relationships and the calculated results are analyzed in Tables I−IV. They allow us to conclude that the derivatives of the dipole moment function in case of completely symmetric isotopic substitution change only insignificantly. Therefore, for practical calculations and estimates of the line intensities it is allowable to use the same expansion of the dipole moment function in the normal coordinates for isotopes $^{16}O_3$, $^{17}O_3$, and $^{18}O_3$. The difference between the values of the derivative μ_x^{33} may be explained by insufficient volume of experimental data on the line intensities from the $2\nu_3$ band of $^{18}O_3$.

APPENDIX

Comparing the expansions of the dimensional and dimensionless normal coordinates of the main species of the molecule in the corresponding coordinates of an arbitrary isotope (see Eq. (6)) and considering that

$Q_i = \sqrt{C/\omega_i}\, q_i$, where Q_i are the dimensional normal coordinates, q_i are the dimensionless normal coordinates, and $C = h/(4\pi^2 c)$, we derive

$$\tilde{\alpha}_i^j = \alpha_i^j \sqrt{\omega_i/\omega_j'} \text{ and } \tilde{\alpha}_i^{jl} = \alpha_i^{jl} \sqrt{C\omega_i/(\omega_j'\,\omega_l')}.$$

Comparing the expansions of the matrix $\varkappa_{\gamma\beta}$ (see Eq. (5)) in the dimensional and dimensionless normal coordinates, we obtain

$$\tilde{\varkappa}_{\alpha\beta}^{0} = \varkappa_{\alpha\beta}^{0}, \quad \tilde{\varkappa}_{\alpha\beta}^{i} = \varkappa_{\alpha\beta}^{i}\sqrt{C/\omega_i}, \text{ and } \tilde{\varkappa}_{\alpha\beta}^{ij} = \varkappa_{\alpha\beta}^{ij}\, C/\sqrt{\omega_i\,\omega_j}.$$

Here, the coefficients with tilde atop denote the dimensionless parameters.

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