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Molecular Dynamics, Root-Mean-Square Amplitudes, Statistical Thermodynamics, and Molecular Polarizability for the Isotopic Species of Dioxygen Monofluoride*

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With 2 Figures

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A brief survey of vibrational spectral studies for the four isotopic species of dioxygen monofluoride has been made. On the basis of group theoretical considerations, symmetry coordinates have been constructed and kinetic energy matrices (or G matrix elements), potential energy matrices, and secular equations have been derived to calculate the valence force constants. The mean-square amplitudes and root-mean-square amplitudes for both the bonded and nonbonded atom pairs have been calculated at the room temperature. On the basis of a rigid rotator and harmonic oscillator model, enthalpy function, free enthalpy function, entropy, and heat capacity have been calculated from 200 to 2000 °K for all the four isotopic species. On the basis of a delta-function potential model based on the variational method and delta-function electronic wave functions, the bond parallel components, the bond perpendicular components, the contribution by the nonbonding electrons, and the average molecular polarizability have been calculated. The results obtained from these studies clearly confirm a double bond character for the oxygen—oxygen distance and a bond order of less than one-half for the oxygen—fluorine distance. The results have been discussed in relation to the nature of the two characteristic bonds involved in this molecular system.

Introduction

All the existing triatomic molecules may in general be classified into six categories, namely, a linear symmetrical $y—x—y$ molecule with the point group $D_{\infty h}$, a bent symmetrical $y\diagup^{x}\diagdown y$ molecule with

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the point group C_{2V}, a linear asymmetrical x—y—z molecule with the point group $C_{\infty v}$, a bent asymmetrical $x\diagup^{y}\diagdown z$ molecule with the point group C_S, a linear asymmetrical x—x—y molecule with the point group $C_{\infty V}$, and a bent asymmetrical molecule with the point group C_S. The typical molecules representing these categories are carbon dioxide, water, hydrogen cyanide, nitrosyl fluoride, nitrous oxide, and dioxygen monofluoride, resp. Various theories have been proposed by many investigators[1, 2] and applied to hundreds of molecules of these categories except the last one for the determination of molecular dynamics, root-mean-square amplitudes, thermodynamics and other related properties. This paper deals with dioxygen monofluoride of the last category.

Among the various halogen containing oxides, the most interesting compound, dioxygen monofluoride, has nineteen valence electrons with many unusual properties, notably, a strong double bond character for the oxygen—oxygen distance, a bond order of less than one-half for the oxygen—fluorine distance, and an apparent lack of reactivity.

The preparations, physico-chemical properties, and infrared absorption spectra for the four isotopic species of dioxygen monofluoride were studied and fundamental frequencies were assigned by *Noble* and *Pimentel*[3], and by *Spratley*, *Turner*, and *Pimentel*[4]. It is aimed here to study the molecular dynamics, root-mean-square amplitudes, statistical thermodynamics, and atomic, bond, and molecular polarizabilities of this molecule. The importance of undertaking such studies is that the results of the present investigation should be very useful in future for (a) the evaluation of normal frequencies in other related molecules having similar chemical bonds, (b) the interpretation of the results of electron diffraction studies, (c) the interpretation of the results of experimental entropies and heat capacities at a pressure of one atmosphere for the ideal gaseous state, (d) testing the utility of the delta-function potential model in other simple as well as complex systems, and (e) the interpretation of the results of experimental refractive index and molar refractions.

Molecular Dynamics

Dioxygen monofluoride possessing an asymmetrical structure with the symmetry point group C_S gives rise, according to the relevant symmetry considerations and selection rules[1], to three vibrational degrees of freedom constituting only three fundamental frequencies, namely, ν_1 the frequency corresponding to the oxygen—oxygen stretching vibration, ν_2 to the oxygen—fluorine stretching vibration, and ν_3 to the bending of the molecule. All are allowed in both the infrared absorption and Raman spectra. The normal modes of oscillation for a molecule of the present study are given by *Wu*[5]. The equilibrium internuclear distances O=O and O—F are being respresented by the symbols R and D, respectively, and similarly, the equilibrium interbond angle $O{=}\widehat{O}{-}F$ by the symbol θ'. On the basis of the group theoretical consideration postulated by *Wilson*[6], the following symmetry coordinates under the A′ symmetry species are constructed: $S_1 = d$, $S_2 = r$, and $S_3 = \sqrt{RD}\,\theta$, where d, r, and θ are the internal coordinates (deviations from the equilibrium values of D, R, and θ'). Here, the angle displacement is multiplied by the equilibrium bond lengths in order to keep the dimensions of the molecular dynamics and mean-square amplitudes referring to the angle bending the same as those of the bonded atom pairs. On the basis of the above symmetry coordinates, the matrix elements related to the kinetic energy were obtained, and they are given under the A′ symmetry species as follows:

$$
\begin{aligned}
G_{11} &= \mu_O + \mu_F \\
G_{12} &= G_{21} = \mu_O \cos\theta \\
G_{13} &= G_{31} = -\mu_O \sin\theta \\
G_{22} &= 2\,\mu_O \\
G_{23} &= G_{32} = -(r/d)\,\mu_O \sin\theta \\
G_{33} &= \mu_O[(r/d)^2 - 2\,(r/d)\cos\theta + 2] + \mu_F\,(r/d)^2
\end{aligned}
$$

where μ_O and μ_F are the reciprocal masses of the oxygen and fluorine atoms, respectively. On the basis of the above symmetry coordinates, the F matrix elements related to the potential energy were obtained, and they are given under the A′ symmetry species as follows: $F_{11} = f_d$, $F_{12} = F_{21} = f_{rd}$, $F_{13} = F_{31} = f_{d\theta}$, $F_{22} = f_r$, $F_{23} = F_{32} = f_{r\theta}$, and $F_{33} = f_\theta$, where f_d is the force constant due to the O—F stretching, f_r the force constant due to the O = O stretching, f_θ the force constant due to the $O{=}\widehat{O}{-}F$ bending, f_{rd} the force constant due to the interaction of O—F and O = O stretchings, $f_{d\theta}$ the force constant due to the interaction of O—F stretching and $O{=}\widehat{O}{-}F$ bending, and $f_{r\theta}$ the force constant due to the interaction of O=O stretching and $O{=}\widehat{O}{-}F$ bending. The fundamental frequencies used for the present calculations are those given by *Noble* and *Pimentel*[3] and by *Turner* and *Pimentel*[4]; and their values for the four isotopic species of dioxygen monofluoride are given as follows:

For the $^{16}O^{16}O^{19}F$ molecule

$\nu_1 = 1495.0\ \mathrm{cm}^{-1}$, $\nu_2 = 584.5\ \mathrm{cm}^{-1}$, and $\nu_3 = 376.0\ \mathrm{cm}^{-1}$.

For the $^{18}O^{18}O^{19}F$ molecule

$\nu_1 = 1411.7\ \mathrm{cm}^{-1}$, $\nu_2 = 560.1\ \mathrm{cm}^{-1}$, and $\nu_3 = 366.0\ \mathrm{cm}^{-1}$.

For the $^{18}O^{16}O^{19}F$ molecule

$\nu_1 = 1455.1\ cm^{-1}$, $\nu_2 = 581.9\ cm^{-1}$, and $\nu_3 = 368.0\ cm^{-1}$.

For the $^{16}O^{18}O^{19}F$ molecule

$\nu_1 = 1452.8\ cm^{-1}$, $\nu_2 = 562.7\ cm^{-1}$, and $\nu_3 = 374.4\ cm^{-1}$.

Since the molecular structural data have not yet been experimentally determined for dioxygen monofluoride, the molecular parameters of dioxygen difluoride[4] were transferred to dioxygen monofluoride and their values are 1.575 Å for the O—F distance, 1.217 Å for the O=O distance, and 109°30′ for the $O{=}\widehat{O}{-}F$ interbond angle, respectively. On the basis of the group theoretical considerations[6], the secular equations giving the normal frequencies in cm^{-1}, molecular structural data, kinetic energy matrices, and potential energy matrices, have then been solved. The fundamental frequencies of the isotopic species facilitated the solution of the secular equations. The evaluated values of valence force constants in 10^5 dynes/cm for dioxygen monofluoride are given as follows:

$$f_d = 1.526,\ f_r = 10.548,\ f_\theta = 1.108,\ \text{and}\ f_{rd} = 1.486.$$

The value of f_r is very close to 11.43 and 11.8 obtained for O_2 and the bond order must be close to two[7, 8]. The value of f_r obtained here is twice the value of 4.59 obtained for the O—O distance of hydrogen peroxide[9]. All these clearly establish a double bond character for the oxygen—oxygen distance of dioxygen monofluoride in line with earlier studies[8]. The value of f_d obtained here is relatively smaller to the values of 4.05 and 3.95 for the O—F distance of difluoro monoxide[7, 8]. These clearly establish a bond order of less than one-half for the oxygen-fluorine distance of dioxygen monofluoride. The value of f_θ obtained here is close to the bending force constant 1.02 obtained for hydrogen peroxide[9]. These values can be transferred to other molecules having similar chemical bonds for evaluating the normal frequencies.

Root-Mean-Square Amplitudes

On the basis of the symmetry coordinates given above, the symmetrized mean-square amplitude matrices for dioxygen monofluoride under the symmetry species A′ are given as follows: $\Sigma_{11} = \sigma_d$, $\Sigma_{12} = \Sigma_{21} = \sigma_{rd}$, $\Sigma_{13} = \Sigma_{31} = \sigma_{d\theta}$, $\Sigma_{22} = \sigma_r$, $\Sigma_{23} = \Sigma_{32} = \sigma_{r\theta}$, and $\Sigma_{33} = \sigma_\theta$, where σ_d is the mean-square amplitude due to the O—F bond, σ_r the mean-square amplitude due to the O=O bond, σ_θ the mean-square amplitude to the bending of the molecule, and σ_{rd}, $\sigma_{r\theta}$ and $\sigma_{d\theta}$ are the respective interaction quantities. The mean-square amplitude σ_t due to the nonbonded atom pair O ---- F has been obtained as a linear combination of the other quantities due to the bonded atom pairs and bending of the molecule, and given as follows: $\sigma_\tau = (\sigma_r + \sigma_d) \sin^2 (\theta/2) + \sigma_\theta \cos^2 (\theta/2) + 2\,\sigma_{rd} \sin^2 (\theta/2) + 2\,(\sigma_{d\theta} + {} + \sigma_{r\theta}) \sin (\theta/2) \cos (\theta/2)$.

The basic equation $| \Sigma\, G^{-1} - E \Delta | = 0$ postulated by *Cyvin*[2] has been used to construct the secular equations, where E is the unity matrix, and Δ is related to the normal frequency ν in the following form:

$$\Delta_i = (h/8\,\pi^2 \nu_i) \coth (h \nu_i \mid 2\,\varkappa T).$$

Here, h is the *Planck*'s constant, $\varkappa$ the *Boltzmann* constant, and T the absolute temperature. The secular equations giving the normal frequencies in terms of the mean-square amplitudes were constructed at 298 °K with help of the kinetic energy matrices, symmetrized mean-square amplitude matrices, vibrational data for the four isotopic species, and structural data given above, and then solved. The evaluated values of the mean-square amplitudes in Å^2 at 298 °K are given as follows: $\sigma_d = 0.0048442$, $\sigma_r = 0.0013838$, $\sigma_\theta = 0.0097835$, $\sigma_{rd} = 0.0012347$, and $\sigma_t = 0.0061623$. The value of the mean-square amplitude quantity due to the bending of the molecule is much larger than those of all other quantities. Similarly, the value of the quantity due to the nonbonded atom pair is larger than those of the other bonded atom pairs. The value of the quantity due to the O—F bond is larger than that of the O=O bond. The largest value of the mean-square amplitudes is the one due to the bending of the molecule (σ_θ), whereas the smallest value of the force constants is the one due to the bending of the molecule (f_θ). The corresponding calculated values of the root-mean-square amplitudes in Å at 298 °K are given as follows: 0.0696 for the O—F bond, 0.0372 for the O=O bond, and 0.0785 for the O ---- F nonbonded atom pair. The value obtained here for the O=O bond is in good agreement with the values of 0.038 and 0.0389 obtained from electron diffraction studies[10, 11] for O_2 molecule. The value obtained here for the O—F bond is much larger than the value of 0.0510 obtained for oxygen difluoride[2], and this confirms a bond order of less than one-half for the oxygen—fluorine distance of dioxygen monofluoride. The values presented here can be transferred to other similar molecules for the evaluation of normal frequencies, and for the interpretation of the results of electron diffraction studies.

Statistical Thermodynamics

In the field of molecular spectroscopy, the infrared absorption and Raman scattering provide valuable information on the accurate assignments of the fundamental frequencies of molecules and ions in the ground as well as many excited states, and on the other vibrational constants. Similarly, the microwave, electron diffraction, neutron diffraction and X-ray diffraction studies determine the structures of molecules and crystals, and yield very reliable values of molecular constants. One of the best applications of the study of infrared absorption and Raman spectra of polyatomic molecules and other molecular structural data is to compute statistically the thermodynamic functions, namely, enthalpy function $(H^0 - H_O{}^0)/T$, free enthalpy function $(F^0 - H_O{}^0)/T$, entropy S^0, and heat capacity $C^0{}_p$. A rigid rotator and harmonic oscillator approximation are assumed and all the four thermodynamic quantities have been computed for a gas in the thermodynamic standard gaseous state of unit fugacity (one atmosphere) for the temperature range 200 °K—2000 °K. The vibrational, translational, and rotational contributions to the total thermodynamic quantities have been computed.

From the molecular structural data, the rotational and translational contributions to the entropy, heat capacity, and free energy function for one mole of a perfect gas at a pressure of one atmosphere were obtained from the following:

$$S_{tr}{}^0 + S_r{}^0 = 2.2868\,(8 \log T + 3 \log M + \log I_{xx} I_{yy} I_{zz} - 2 \log \sigma) - 7.6965$$
$$-(F_{tr}{}^0 + F_r{}^0 - H_o{}^0)/T = S_{tr} + S_r{}^0 - 4R$$
$$\text{and } (C_p{}^0)_{tr} + (C_p{}^0)_r = (H_{tr}{}^0 + H_r{}^0 - H_o{}^0)/T = 4R$$

where S, F, C_p, H, tr, r, T, M, and σ stand for entropy, free energy, heat capacity at constant pressure, enthalpy, translational part, rotational part, temperature in degrees Kelvin, total mass of the molecule, and molecular Symmetry number. I_{xx}, I_{yy}, and I_{zz} are the principal moments of inertia in atomic mass units times Å^2 along the x-axis, y-axis, and z-axis, resp. The value of the gas constant R is 1.9872 cal/degree mole. These contributions due to translation and rotation were added to the contributions due to vibration in order to obtain the total contributions to the free energy function, $-(F^0 - H_O{}^0)\,/\,T$, and the entropy, S^0, at a pressure of one atmosphere.

The principal moments of inertia were calculated from the same structural data used for the calculation of molecular dynamics, and their values for all the four isotopic species are given as follows:

For the $^{16}O^{16}O^{19}F$ molecule:

$I_{xx} =$ 6.0182 AMU Å^2 (9.9970×10^{-40} g cm^2)
$I_{yy} =$ 51.6534 AMU Å^2 (85.8030×10^{-40} g cm^2)
$I_{zz} =$ 45.6532 AMU Å^2 (75.8060×10^{-40} g cm^2)

For the $^{18}O^{18}O^{19}F$ molecule:

$I_{xx} = 6.2780$ AMU Å^2 (10.4286×10^{-40} g cm^2)
$I_{yy} = 57.6176$ AMU Å^2 (95.7103×10^{-40} g cm^2)
$I_{zz} = 51.3396$ AMU Å^2 (85.2817×10^{-40} g cm^2)

For the $^{16}O^{18}O^{19}F$ and $^{18}O^{16}O^{19}F$ molecules:

$I_{xx} = 6.1530$ AMU Å^2 (10.2209×10^{-40} g cm^2)
$I_{yy} = 54.6404$ AMU Å^2 (90.7648×10^{-40} g cm^2)
$I_{zz} = 48.4874$ AMU Å^2 (80.5439×10^{-48} g cm^2).

Table 1. *Enthalpy Function, Free Enthalpy Function, Entropy, and Heat Capacity of* $^{16}O^{16}O^{19}F$ *for the Ideal Gaseous State at a Pressure of One Atmosphere.* (All the quantities are in cal/degree mole)

T (°K)	$(H^0 - H_0{}^0)/T$	$-(F^0 - H_0{}^0)/T$	S^0	$C_p{}^0$
200	8.4854	47.8686	56.3540	9.6887
273.16	8.9240	50.5832	58.5072	10.4785
298.16	9.0604	51.3670	60.4279	10.6878
300	9.0714	51.4231	60.4945	10.7039
400	9.5686	54.1048	63.6734	11.3776
500	10.0287	56.3325	66.3612	11.9199
600	10.3337	58.1362	68.4699	12.2776
700	10.6338	59.7503	70.3841	12.5826
800	10.8858	61.1739	72.0597	12.8143
900	11.1147	62.4793	73.5940	12.9987
1000	11.3126	63.6650	74.9776	13.1432
1100	11.4833	64.7509	76.2342	13.2565
1200	11.6353	65.7546	77.3899	13.3485
1300	11.7667	66.6715	78.4382	13.4226
1400	11.8881	67.5611	79.4492	13.4812
1500	11.9978	68.3874	80.3852	13.5337
1600	12.0987	69.1739	81.2726	13.5766
1700	12.1856	69.9105	82.0941	13.6114
1800	12.2627	70.6028	82.8655	13.6404
1900	12.3384	71.2727	83.6111	13.6674
2000	12.4028	71.9032	84.3060	13.6883

Assumed in the computations were a symmetry number of 1, singlet ground electronic state, and chemical atomic weights. Neglected in the calculations were contributions due to the centrifugal distortion, isotopic mixing, nuclear spins, and interaction between vibration and rotation, since the contributions of these quantities are negligibly small compared to the total thermodynamic quantities due to vibration, rotation, and translation. The computed values of all the four thermodynamic quantities in calories per degree mole for all the four isotopic species are given in Tables from 1 to 4 at the temperatures 200–2000 °K. The constant term $R \ln 2 = 1.38$ calories per degree mole should be added to S^0 and $-(F^0 - H_0{}^0)/T$ in all the four tables in order to account for the doublet character of the ground electronic state of these four isotopic species. The values presented here are the most reliable ones, and should be very useful for the evaluation of normal frequencies in other related molecules having similar chemical bond, and for the interpretation of the results of experimental entropies and heat capacities for the ideal gaseous state at a pressure of one atmosphere.

Table 2. *Enthalpy Function, Free Enthalpy Function, Entropy, and Heat Capacity of* $^{18}O^{18}O^{19}F$ *for the Ideal Gaseous State at a Pressure of One Atmosphere.* (All the quantities are in cal/degree mole)

T (°K)	$(H^0 - H_0{}^0)/T$	$-(F^0 - H_0{}^0)/T$	S^0	$C_p{}^0$
200	8.4983	48.4486	56.9469	9.7012
273.16	8.9468	51.1699	60.1167	10.5237
298.16	9.0764	51.9545	61.0309	10.7145
300	9.0776	52.0028	61.0804	10.7206
400	9.7064	54.7901	64.4965	11.5499
500	10.0082	56.8782	66.8864	11.9489
600	10.3657	58.7307	69.0964	12.3509
700	10.6745	60.3576	71.0321	12.6542
800	10.9309	61.7879	72.7188	12.8809
900	11.1602	63.0954	74.2556	13.0576
1000	11.3527	64.2661	75.6188	13.1945
1100	11.5294	65.3724	76.9018	13.3024
1200	11.6830	66.3832	78.0662	13.3906
1300	11.8170	67.3238	79.1408	13.4600
1400	11.9288	68.1754	80.1042	13.5144
1500	12.0431	69.0307	81.0738	13.5633
1600	12.7366	69.8165	81.9571	13.6019
1700	12.2283	70.5600	82.7883	13.6350
1800	12.3038	71.2559	83.5597	13.6619
1900	12.3738	71.9100	84.2838	13.6847
2000	12.4485	72.5877	85.0362	13.7080

Molecular Polarizability

The delta-function potential model based on the variational method and delta-function electronic wave functions was first applied by *Rüdenberg* and his associates[13, 14] in studying the properties of chemical bonds. Later, *Frost*[15] applied a delta-function potential model of chemical binding to the calculation of energies of various systems with introduction of a branching condition[16] followed by *Lippincott*[17] with a semi-empirical delta-function potential model. *Lippincott* and

Dayhoff[18] used the semi-empirical delta-function techniques in predicting the vibrational frequencies, anharmonicities, bond dissociation energies, and equilibrium internuclear distances. Later, *Lippincott* and *Stutman*[19] applied this semi-empirical delta-function potential model in generating component polarizabilities in order to compute

Table 3. *Enthalpy Function, Free Enthalpy Function, Entropy, and Heat Capacity of* $^{16}O^{18}O^{19}F$ *for the Ideal Gaseous State at a Pressure of One Atmosphere.* (All the quantities are in cal/degree mole)

T (°K)	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
200	8.4781	48.2012	56.6793	9.6642
273.16	8.9089	50.9099	59.8188	10.4571
298.16	9.0412	51.6918	60.7330	10.6479
300	9.0534	51.7473	60.8007	10.6815
400	9.8147	54.8129	64.6276	11.5225
500	9.9734	56.6011	66.5745	11.9044
600	10.3297	58.4520	68.7817	12.3046
700	10.6366	60.0711	70.7077	12.6116
800	10.9026	61.5177	72.4203	12.8467
900	11.1238	62.8004	73.9242	13.0756
1000	11.3208	63.9830	75.3038	13.1655
1100	11.4917	65.0667	76.5584	13.2764
1200	11.6506	66.0884	77.7390	13.3680
1300	11.7871	67.0407	78.8278	13.4387
1400	11.9072	67.9141	79.8213	13.4985
1500	12.0119	68.7193	80.7312	13.5472
1600	12.1041	69.4835	81.5876	13.5854
1700	12.1898	70.2065	82.3963	13.6201
1800	12.2760	70.9325	83.2085	13.6507
1900	12.3491	71.6096	83.9587	13.6754
2000	12.4229	72.2567	84.6796	13.6994

the average molecular polarizabilities for both diatomic and polyatomic molecules of only non-transition elements. Recently, *Nagarajan*[20–25] introduced a general method based on the semi-empirical delta-function potential model, and computed the component polarizabilities and average molecular polarizabilities of many diatomic and polyatomic molecules of both transition and non-transition elements. This model gives explicit expressions for the parallel and perpendicular components and average molecular polarizabilities for both diatomic and polyatomic molecules. The molecular polarizability is composed mainly of bond parallel components obtainable from molecular delta-function potential model, and bond perpendicular components obtainable from the atomic delta-function polarizabilities. The polarizability contributions from the bonding electrons and those from the nonbonding electrons are clearly distinguished. In addition, corrections to the parallel and perpendicular components are made to compensate for polarity effects. The same method has been applied here for dioxygen monofluoride.

The delta-function strengths A in atomic units, atomic polarizabilities in 10^{-25} cm^3, and the parameter c values in atomic units for the end oxygen and fluorine atoms are given as follows:

Table 4. *Enthalpy Function, Free Enthalpy Function, Entropy, and Heat Capacity of* $^{18}O^{16}O^{91}F$ *for the Ideal Gaseous State at a Pressure of One Atmosphere.* (All the quantities are in cal/degree mole)

T (°K)	$(H^0 - H_0{}^0)/T$	$-(F^0 - H_0{}^0)/T$	S^0	$C_p{}^0$
200	8.4763	48.1968	56.6731	9.6436
273.16	8.9033	50.9065	59.8098	10.4319
298.16	9.0385	51.6892	60.7277	10.6290
300	9.0452	51.7427	60.7879	10.6560
400	9.5404	54.4156	63.9560	11.3547
500	9.9613	56.5922	66.5535	11.8897
600	10.3170	58.4427	68.7597	12.2855
700	10.6151	60.0420	70.6571	12.5791
800	11.8808	61.4853	72.3661	12.8320
900	11.1075	62.7779	73.8854	13.0144
1000	11.3070	63.9584	75.2654	13.0939
1100	11.4851	65.0568	76.5419	13.5259
1200	11.6361	66.0569	77.6930	13.3630
1300	11.7714	66.9892	78.7606	13.4347
1400	11.8885	67.8557	79.7442	13.4899
1500	11.9986	68.6990	80.6976	13.5411
1600	12.1003	69.4828	81.5831	13.5842
1700	12.1904	70.2202	82.4126	13.6195
1800	12.2977	70.9704	83.2681	13.6631
1900	12.3406	71.5668	83.9074	13.6740
2000	12.4038	72.1942	84.5980	13.6941

$$A_O = 1.00,\ A_F = 1.065,\ \alpha_O = 5.92,\ \alpha_F = 4.90,\ c_O = 4.899, \text{ and } c_F = 5.635.$$

These values are for the bonds of diatomic molecules. On the basis of the delta-function potential model, the central oxygen atom is considered here for the bonds of a polyatomic molecule. The obtained values of the delta-function strength in atomic units, atomic polarizability in 10^{-25} cm^3, and the parameter c value in atomic units for the central oxygen atom of dioxygen monofluoride are given as follows: $A_O = 0.895$, $\alpha_O = 8.29$, and $c_O = 4.385$. A bond order of one-half for the oxygen-fluorine distance, and a bond order of two for the oxygen—oxygen distance have been considered here in line with the results of molecular dynamics and root-mean-square amplitudes obtained for dioxygen monofluoride. The same molecular structural data used for the calculation of molecular dynamics have been used here.

The contribution to the bond parallel component by the bonding electrons is calculated by using a linear combination of atomic delta-functions representing the two nuclei in the bond, and is expressed as $\alpha_{\parallel b} = 4n\, A_{12}\, (1/a_O)\ (\langle\chi\rangle)^2$ where n is the bond order, A_{12} the root-mean-square delta-function strength of the two nuclei, a_O the radius of the first Bohr orbit of atomic hydrogen, and $\langle\chi^2\rangle$ the mean-square position of a bonding electron which may be expressed as $\langle\chi^2\rangle = (R^2/4) + (1/2\, c_{R_{12}^2})$ where R is the internuclear distance at the equilibrium configuration. The calculated values of the bond parallel components in 10^{-25} cm³ for the O=O and O—F bonds are 20.312, and 14.408, resp.

In case that the bond is of a heteronuclear type, a polarity correction is introduced from the *Pauling*'s expression $\sigma = e^{-(1/4)(x_1 - x_2)^2}$ where x_1 and x_2 are the electronegativities of the atoms 1, and 2, resp. on the *Pauling*'s scale[26]. After introducing the polarity correction, the expression for the bond parallel component is given as $\alpha_{\parallel p} = \sigma \alpha_{\parallel b}$. The polarity correction for a bond with a bond order greater than unity is not made, as the electron density in the bond region is greater. The calculated value of the bond parallel component for only the O—F bond is given as 13.569×10^{-25} cm³. There is no polarity correction necessary here for the O=O bond[26].

The contribution by the nonbonding electrons to the bond parallel components of the whole molecule is calculated from the remaining electrons in the valence shell of each atom not involved in the bonding, and is expressed as $\Sigma\alpha_{\parallel b} = \Sigma f_i\, \alpha_i$, where f_i is the fraction of electrons in the valence shell of the ith atom not involved in the bonding, and α_i the atomic polarizability of the ith atom obtainable from the delta-function strength A_i. The calculated value of the contribution by the nonbonding electrons for dioxygen monofluoride is given as $13.68 \times$ $\times 10^{-25}$ cm³.

The bond perpendicular component of a diatomic molecule is simply the sum of two atomic polarizabilities, i.e., $\alpha_\perp = 2\,\alpha_A$ for a nonpolar A_2 molecule, and $\alpha_\perp = 2\,(x_A{}^2\,\alpha_A + x_A{}^2\,\alpha_B)/(x_A{}^2 + x_B{}^2)$ for an A—B molecule, where x refers to the electronegativity of the atom. Extending this principle, the sum of the perpendicular components of all the bonds in a polyatomic molecule is given as $\Sigma\, 2\,\alpha_\perp =$ $= n_{df}\, (\Sigma\, x_i{}^2\, \alpha_i / \Sigma\, x_i{}^2)$, where n_{df} is the number of residual atomic polarizability degrees of freedom. n_{df} is directly obtained from the geometry of the molecule and the assumption that each atom, if it were bonded, would possess three atomic polarizability degrees of freedom. If an atom forms one bond, one atomic polarizability degree of freedom is lost, i.e., oxygen molecule has four residual atomic polarizability degrees of freedom (Fig. 1). If two bonds are formed from the same atom and exist in a linear configuration (carbon disulfide), three atomic polarizability degrees of freedom are lost. If two bonds are formed from the same atom and exist in a nonlinear configuration (central oxygen in dioxygen monofluoride), four atomic polarizability degrees of freedom are lost (Fig. 2). If three bonds are formed from the same

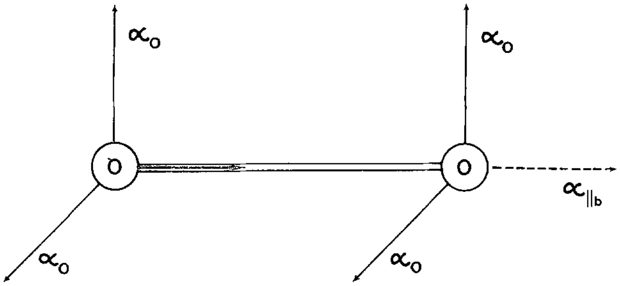

Fig. 1. Residual atomic polarizability degrees of freedom for oxygen molecule

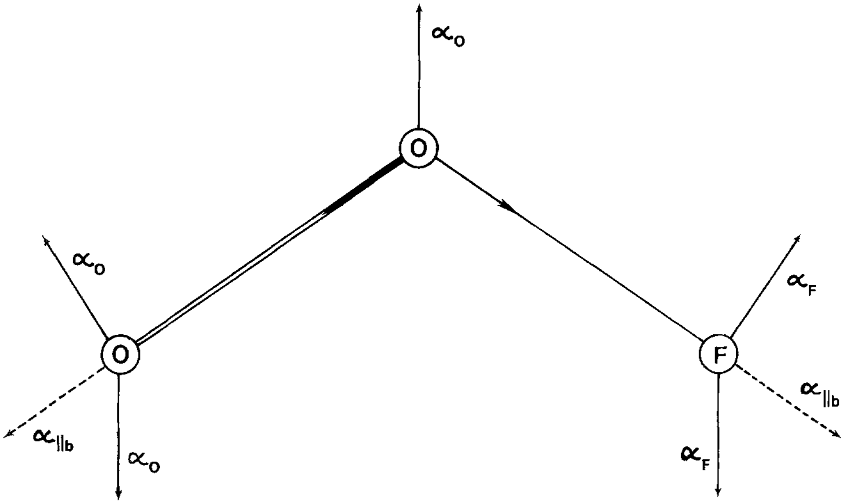

Fig. 2. Residual atomic polarizability degrees of freedom for dioxygen monofluoride

atom and exist in a planar configuration (boron in BF_3), five atomic polarizability degrees of freedom are lost. On the basis of this, the calculated value of the sum of all the perpendicular components for dioxygen monofluoride is given as 31.169×10^{-25} cm³.

On the basis of the delta-function potential model, the average molecular polarizability is obtained in terms of the bond parallel components, contribution by the nonbonding electrons, and bond perpendicular components from the following:

$$\bar{\alpha}_M = (1/3)\,(\Sigma\,\alpha_{\|p} + \Sigma\,\alpha_{\|n} + \Sigma\,2\,\alpha_{\perp}).$$

The calculated value of the average molecular polarizability for dioxygen monofluoride is given as

$$\bar{\alpha}_M = (1/3)\,(33.881 + 13.68 + 31.169) \times 10^{-25}\ \mathrm{cm}^3 = 26.243 \times 10^{-25}\ \mathrm{cm}^3$$

when the polarity correction is not introduced, the calculated value of the average molecular polarizability is given as:

$$\bar{\alpha}_M = (1/3)\,(34.72 + 13.68 + 31.169) \times 10^{-25}\ \mathrm{cm}^3 = 26.523 \times 10^{-25}\ \mathrm{cm}^3.$$

Thus, the polarity correction does not have much effect on the average molecular polarizability. Though the number of nonbonding electrons is greater than that of the bonding electrons, the contribution by the nonbonding electrons to the average molecular polarizability is the smallest of all. The normal O_2 molecule with a double bond character has a bond parallel component of 20.154×10^{-25} cm³ and this value is in good agreement with the value of 20.312×10^{-25} cm³ for the $O{=}O$ bond of dioxygen monofluoride. This strongly confirms a double bond character for the oxygen—oxygen distance of dioxygen monofluoride. It has been found from the previous investigations[20–26] that the oxygen—fluorine distance with a single bond character has a bond parallel component of 17.979×10^{-25} cm³, whereas the value obtained here for the oxygen fluorine distance is extremely low, and confirms the results of molecular dynamics and root-mean-square amplitudes obtained here with a bond order of less than one-half for the oxygen—fluorine distance. The results obtained here should be very useful for the interpretation of the results of refractive index and molar refractions of dioxygen monofluoride.

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